Origins of Initiation Rate Differences in Ruthenium Olefin Metathesis Catalysts Containing Chelating Benzylidenes

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SUPPORTING INFORMATION

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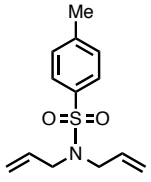
GENERAL INFORMATION

All reactions were carried out in a flask open to air, in dry glassware under an argon atmosphere using standard Schlenk techniques, or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, as specified. Unless otherwise noted, all materials were used as received from commercial sources without further purification. Catalysts **2**, **4**, **S16**, and **S17** and (*E*/*Z*)-1-isopropoxy-4-nitro-2-(prop-1-en-1-yl)benzene (**S20**) were donated by Materia, Inc. All other chemicals were purchased from Aldrich. All bulk solvents were purchased from VWR and used as received. In air- or moisture-sensitive reactions, anhydrous, degassed solvents were used. Anhydrous DMSO was purchased from Aldrich. All other non-deuterated solvents were purified by passage through solvent purification columns. ^{1}H and ^{13}C spectra were recorded on Varian Mercury (300 MHz and 75 MHz, respectively) and Varian Inova (500 MHz and 125 MHz, respectively) instruments. The CD_2Cl_2 that was used for RCM kinetics was distilled over CaH_2 and freeze-pump-thaw degassed (× 3) prior to use, and the purity of the solvent was found to be critical for reproducibility. Solutions of catalysts **5**–**9** for NMR analysis were prepared in a glovebox using freshly opened ampules of CD_2Cl_2 from Cambridge Isotope Laboratories. $CDCl_3$ was handled outside of the glovebox and used as received from Cambridge Isotope Laboratories. All NMR Spectra were internally referenced to $SiMe_4$ or chloroform signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, and b = broad. High-resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were ionized by EI or FAB.

EXPERIMENTAL PROCEDURES

^{1}H NMR RCM Kinetics:



24

***N*,*N*-diallyl-4-methylbenzenesulfonamide (24):**[1,2] To a 250 mL round-bottom flask containing a magnetic stir bar, were added DCM (50 mL), diallylamine (1.23 mL, 10.0 mmol), and triethylamine (1.80 mL, 13.0 mmol). The reaction vessel was cooled to 0 °C in an ice bath, and tosyl chloride (2.48 g, 13 mmol) was added. The reaction was allowed to warm to room temperature and stir for 4 d. The reaction was quenched with H_2O (50 mL), and the biphasic mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with DCM (2 × 50 mL). The organic layers were combined, washed sequentially with 1.0 M HCl solution (100 mL), sat. $NaHCO_3$ solution (100 mL), and brine (100 mL), filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography provided **24** as a colorless oil (2.23 g, 89% yield). Analytical data were in agreement with previous reports.[1,2]

General Procedure for RCM ^{1}H NMR Kinetics with Diene 24:[3–5] In a glovebox, a 0.4 M stock solution of diene **24** (101 mg, 0.4 mmol) in CD_2Cl_2 (1.0 mL solution volume) was prepared. A 0.25 mL aliquot of the 0.4 M was added to an NMR tube, and CD_2Cl_2 (0.75 mL) was added, to obtain 1.0 mL of a 0.1 M solution of **24** in CD_2Cl_2. The NMR tube was tightly capped with a septum. Separately, a 0.01 M stock solution of the ruthenium catalyst (0.01 mmol)

in CD_2Cl_2 (1.0 mL solution volume) was prepared in a septum-topped vial. Both the NMR tube and the vial were removed from the glovebox. The NMR sample was added into an NMR instrument with a temperature controller set to 25 °C, which was then tuned, locked, and shimmed over the course of 5 minutes. The sample was ejected, and 10 µL of the catalyst stock solution ($1 \cdot 10^{-4}$ mmol) was added. The NMR tube was mixed thoroughly (by inverting twice), and placed back in the NMR instrument. The machine was locked, and the experiment was initialized (1 min ± 5 sec after catalyst solution injection). Data acquisition was carried out using the Varian array function. Reaction progress was monitored by integration of the allylic proton signals (consumption of **24** at 3.70 ppm (d, J = 6.0 Hz, 4H) and production of **25** at 4.00 ppm (s, 4H)).[2] All catalysts were measured in triplicate (Charts S1–S5).

Chart S1: RCM ^{1}H NMR kinetic data with catalyst **4**.

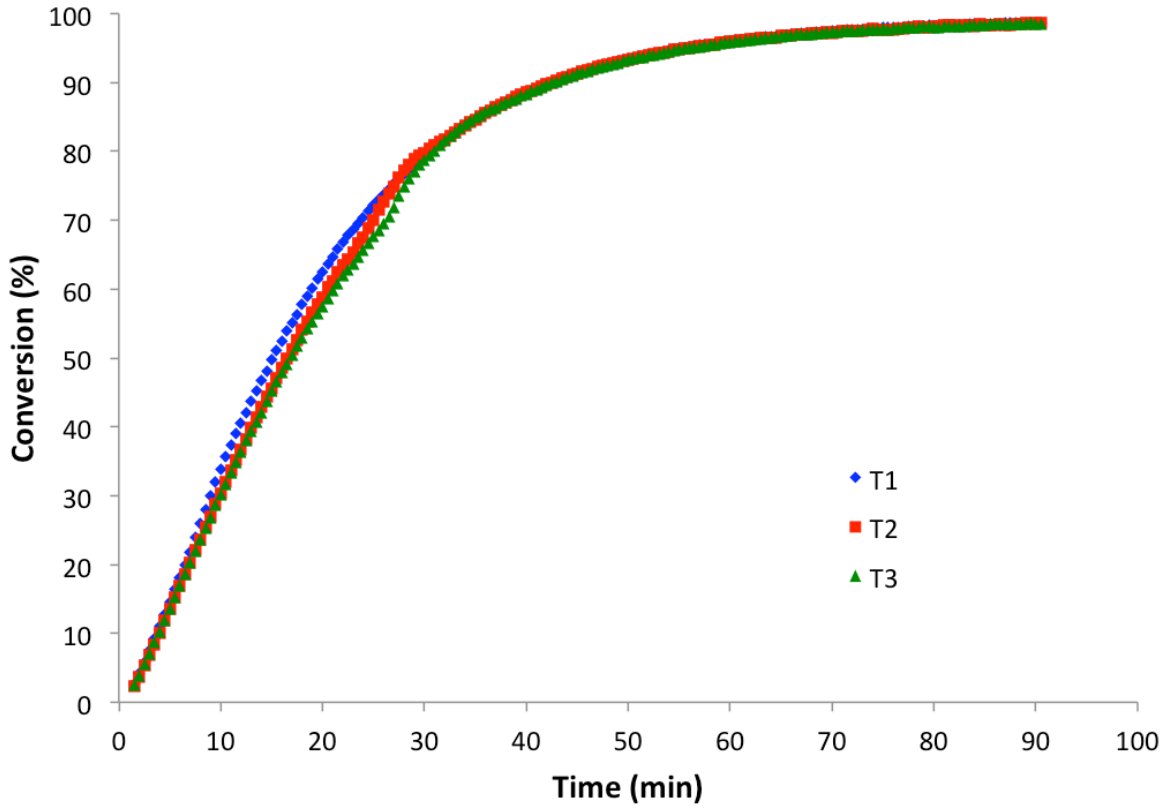


Chart S2: RCM ^{1}H NMR kinetic data with catalyst **9**.

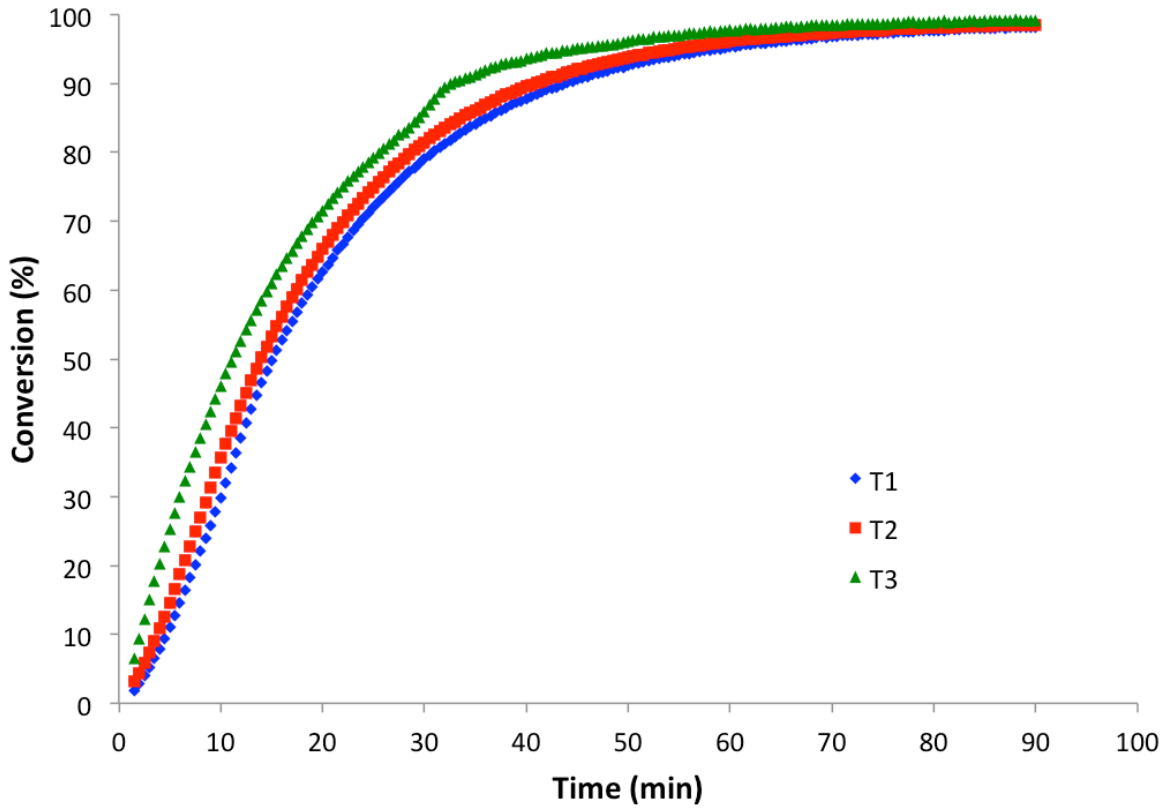


Chart S3: RCM ^{1}H NMR kinetic data with catalyst **10**.

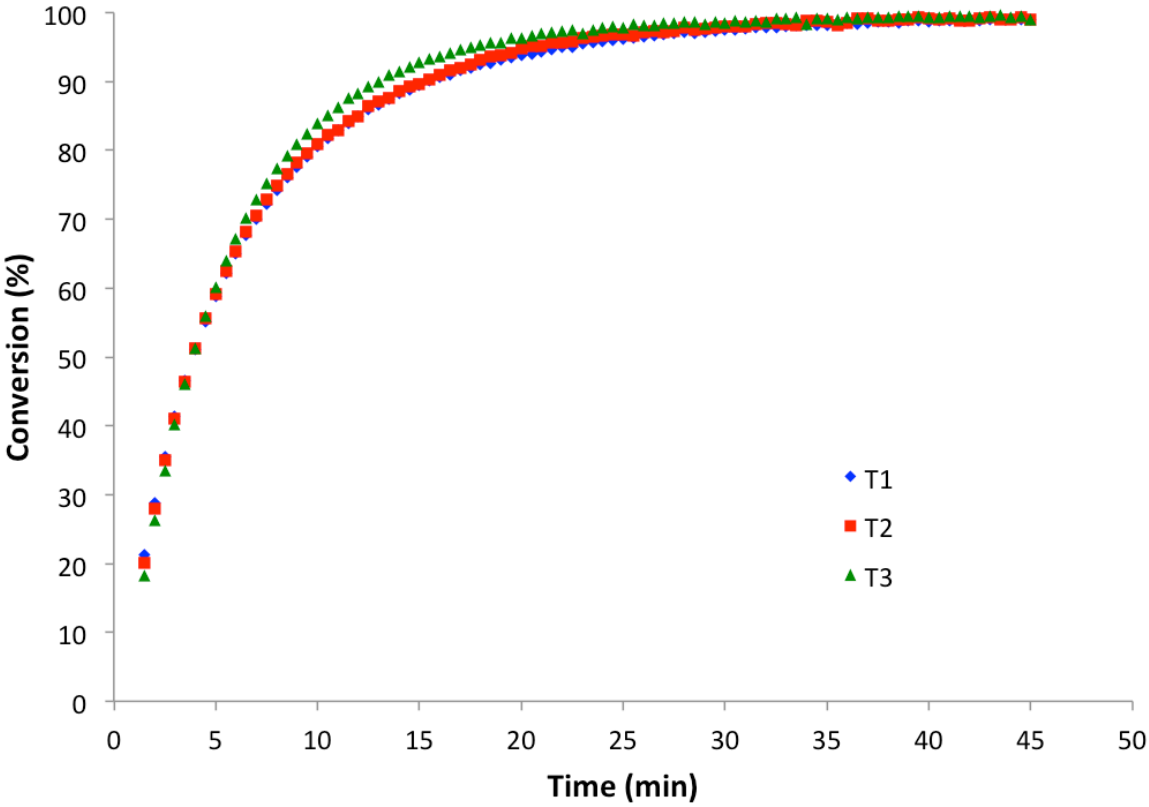


Chart S4: RCM ^{1}H NMR kinetic data with catalyst **11**.

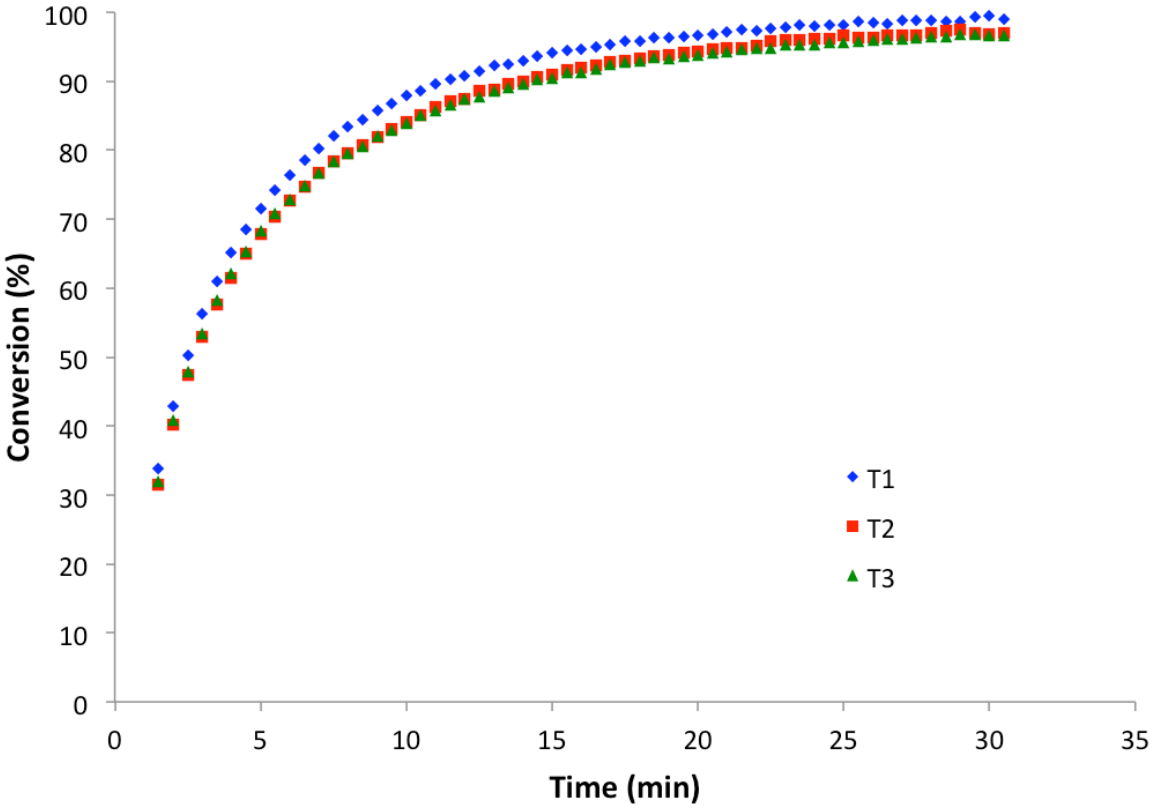
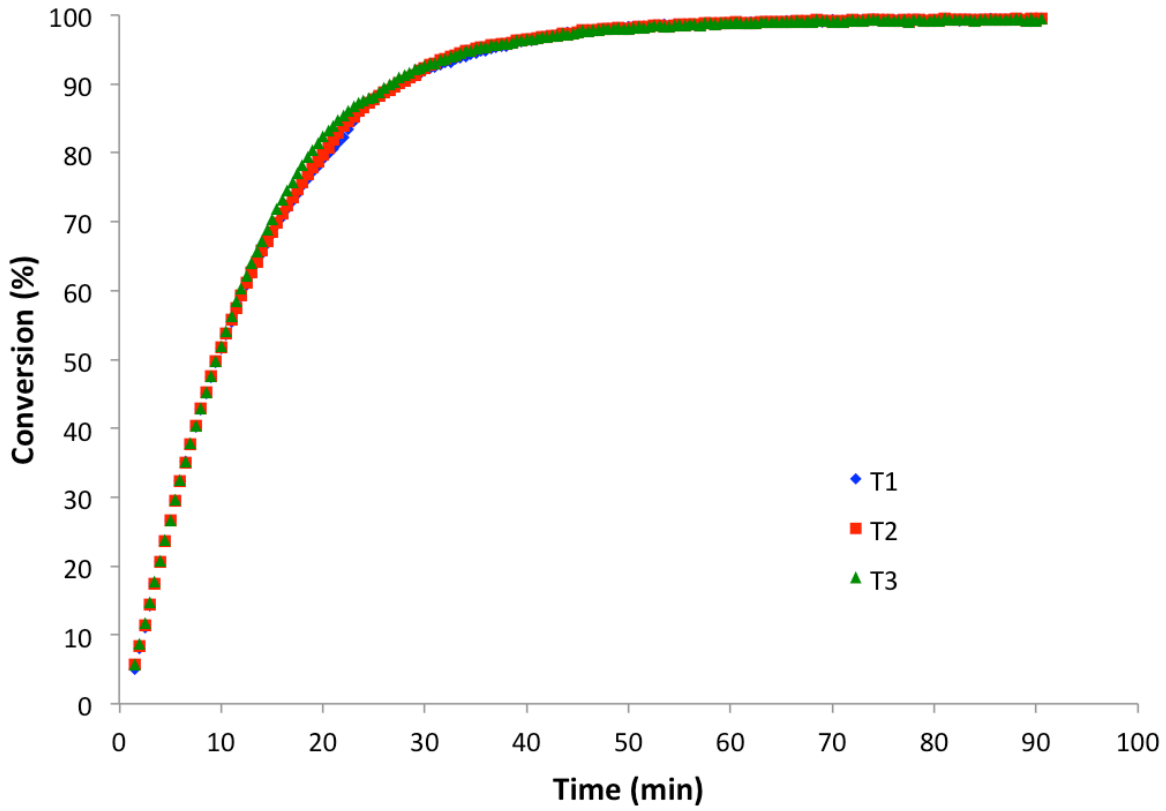


Chart S5: RCM ^{1}H NMR kinetic data with catalyst **12**.



UV/Vis Initiation Kinetics:

Septum-equipped screw-capped quartz cuvettes for UV/Vis were purchased from Starna Cells, Inc. (Item# 1-Q-10-GL14-S). All catalyst solutions were prepared and handled in a glovebox. Cuvettes were tightly sealed, removed from the glovebox, and wrapped with additional parafilm to secure the cap. UV/Vis kinetics experiments were performed on an Agilent HP8452 UV/Vis spectrophotometer with temperature controller and magnetic stir plate. The solution was allowed to equilibrate to the desired temperature (10 °C) for at least 10 min, prior to beginning the experiment. During the experiment, dry air was blown over the faces of the cuvette to prevent condensation.

General Procedure for UV/Vis Initiation Kinetics with BVE:[5–7] In a glovebox, a $1{\cdot}10^{-3}$ M stock solution of the appropriate catalyst (0.01 mmol) in toluene (10.0 mL solution volume) was prepared. A 0.30 mL aliquot of the $1{\cdot}10^{-3}$ M catalyst stock solution was dispensed into a UV/Vis cuvette, and additional toluene (2.7 mL) was added to obtain 3.0 mL of a $1{\cdot}10^{-4}$ M solution of the catalyst in toluene. Separately, a 0.50 M stock solution of butyl vinyl ether (100.2 mg, 1.00 mmol) in toluene (2.0 mL solution volume) was prepared in a septum-topped vial; toluene was added in the glovebox, and butyl vinyl ether was added by syringe outside of the glovebox. Outside of the glovebox, the cuvette was placed in the UV/Vis spectrophotometer and allowed to equilibrate to the desired temperature (10 °C) for at least 10 min, prior to beginning the

experiment. A spectrum was collected to determine λ_{max} for the catalyst. At a catalyst concentration of $1 \cdot 10^{-4}$ M, the absorbance was generally near 1.0 (± 0.2). An aliquot of the butyl vinyl ether stock solution (18 µL, $9.0 \cdot 10^{-3}$ mmol, 30 equiv, $3.0 \cdot 10^{-3}$ M in the reaction solution) was added, and data collection was initialized. Spectra were collected at regular intervals for at least three half-lives (Chart S6). The absorbance value at λ_{max} was plotted against time, and the data were fit to a first-order exponential decay function, from which k_{obs} (k_{init} for the purposes of this paper) was determined (Charts S7 and S8). Other wavelengths (λ_{max} ± 4 nm) gave very similar k_{obs} values. The experiment was repeated in triplicate for each catalyst. The results are summarized in Table S1.

Chart S6: Representative data for a UV/Vis initiation kinetics experiment (catalyst **4**, trial 1).

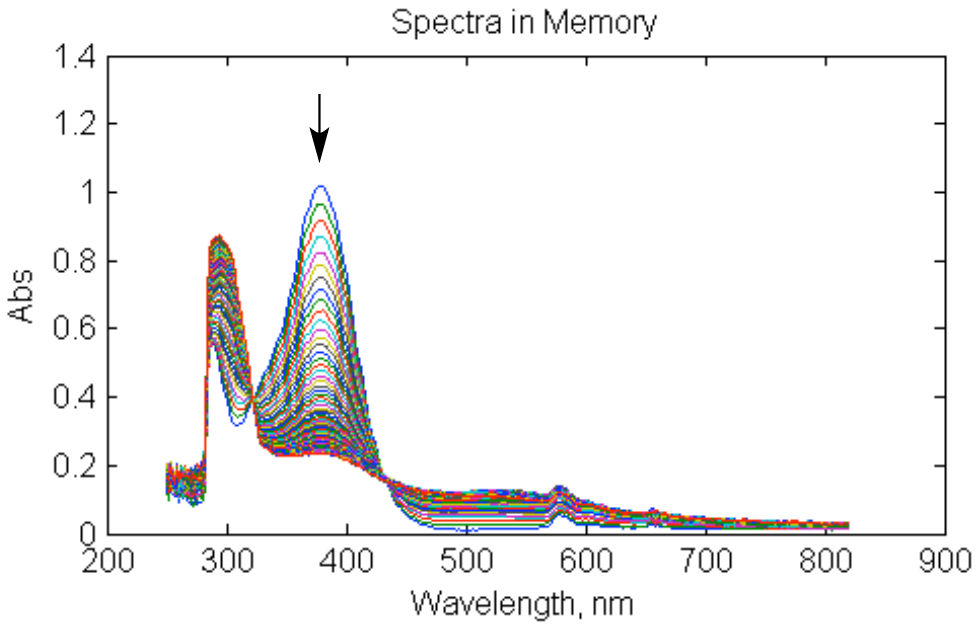


Chart S7: Representative plot of absorbance (λ_{max} = 378 nm) versus time for a UV/Vis initiation kinetics experiment (catalyst **4**, trial 1).

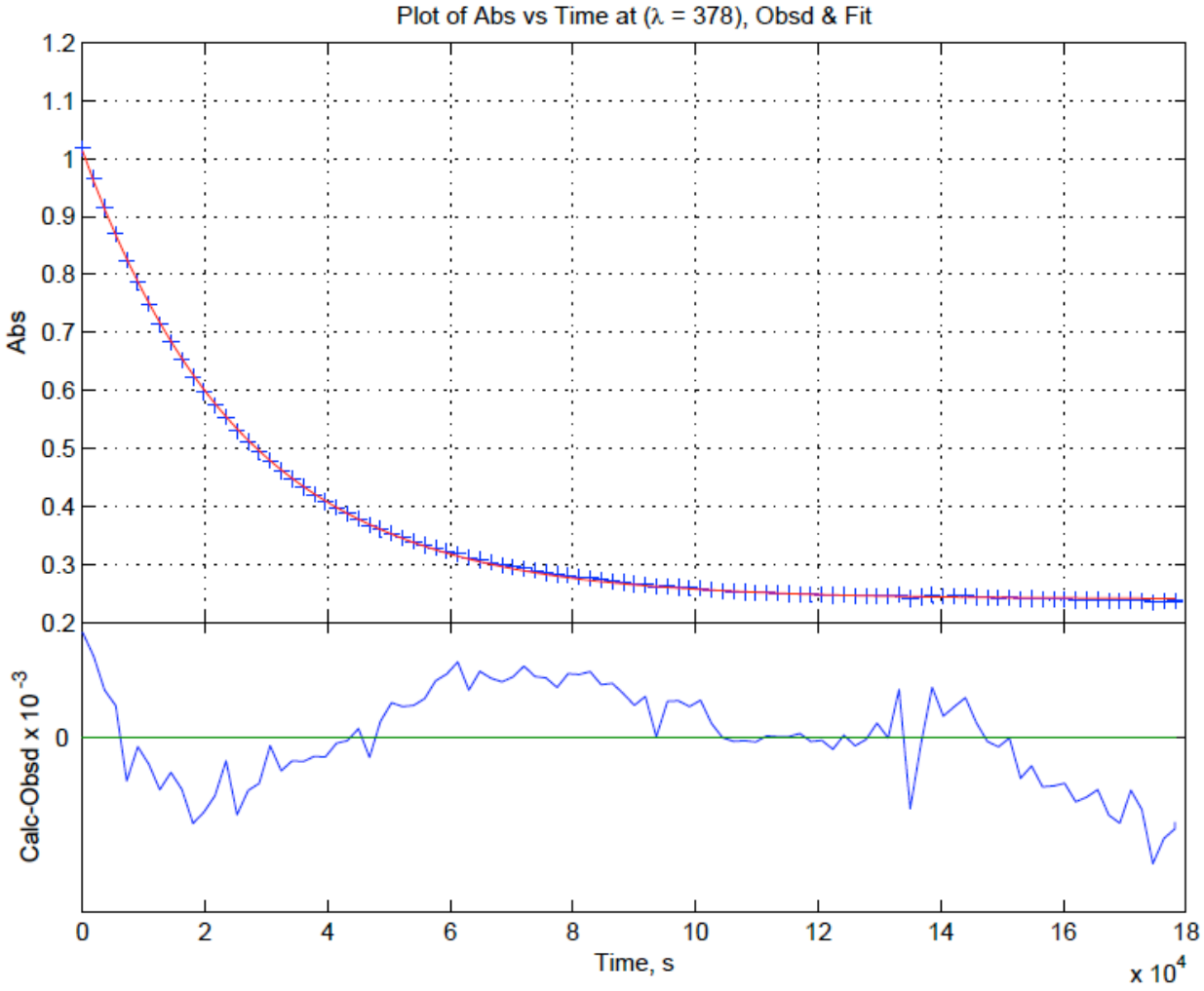


Chart S8: Representative semi-log plot of absorbance (λ_{max} = 378 nm) versus time for a UV/Vis initiation kinetics experiment (catalyst **4**, trial 1).

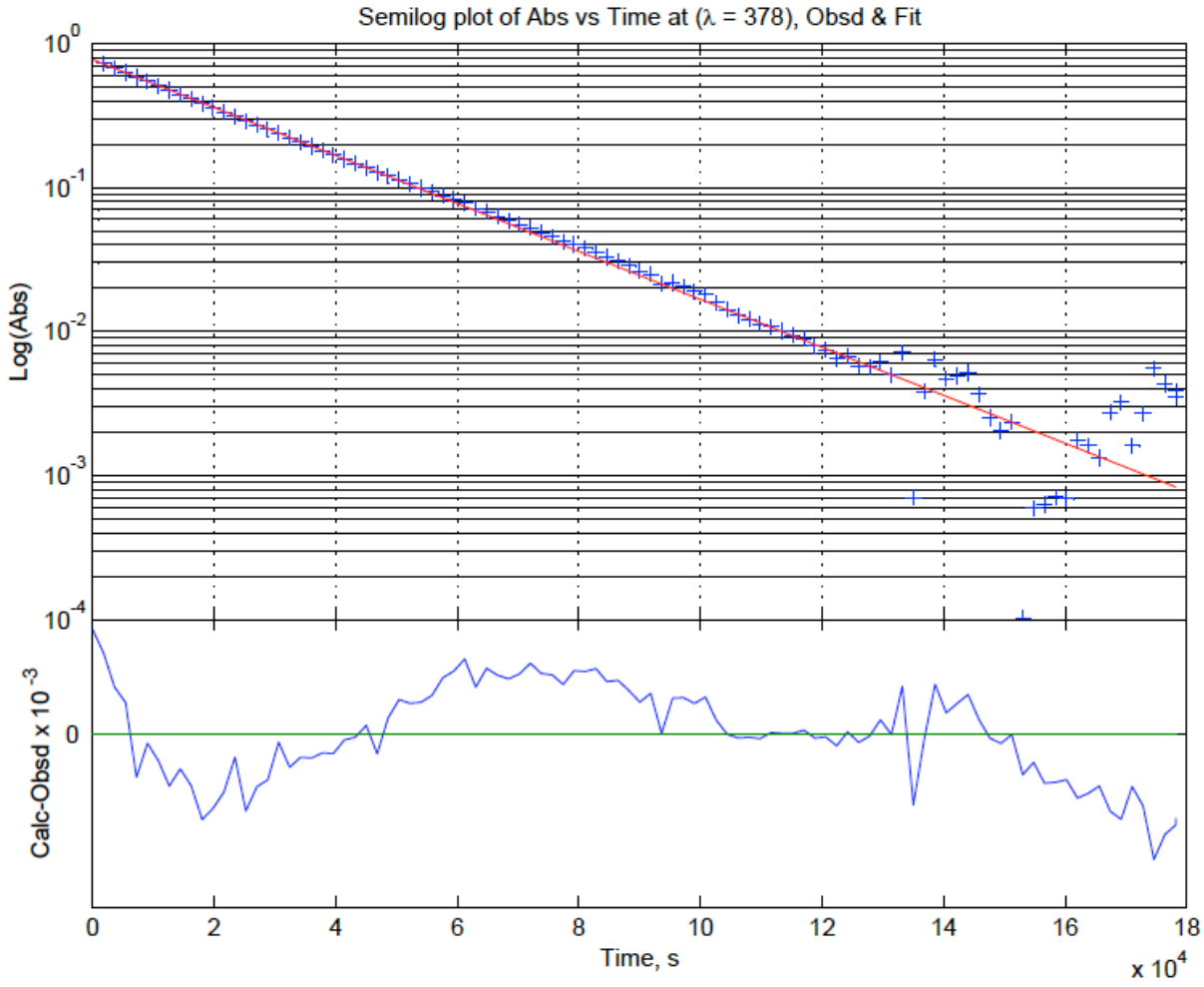
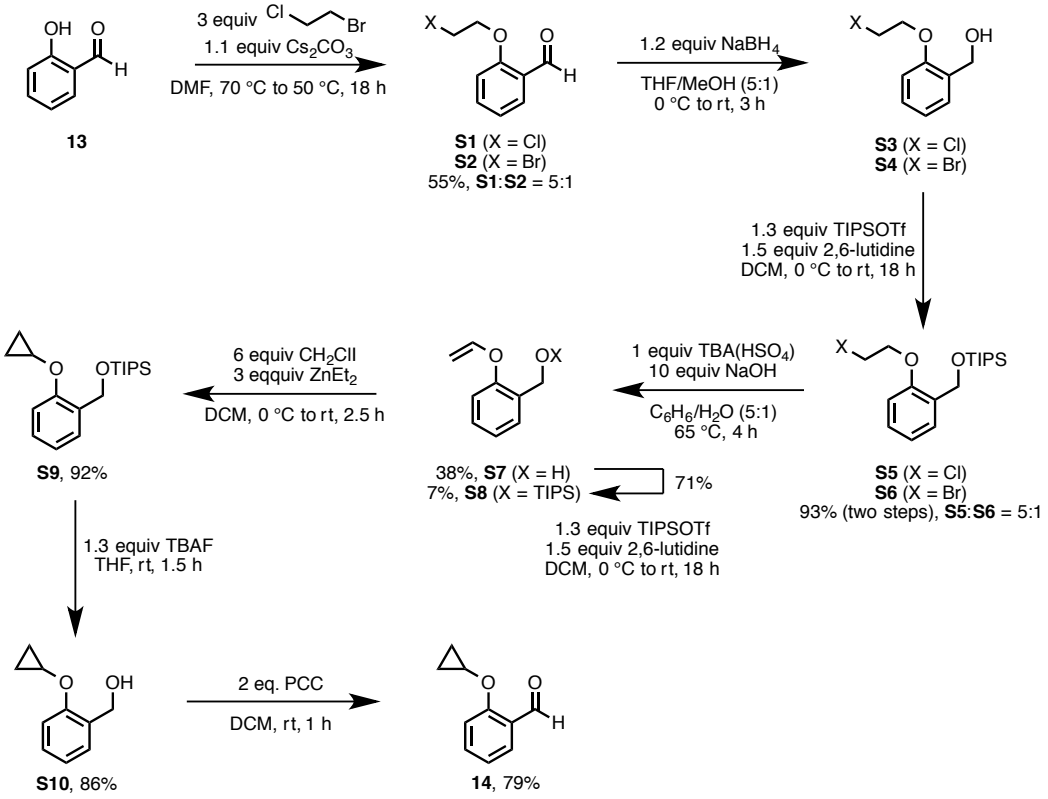


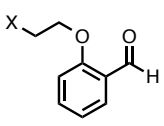
Table S1: Summary of UV/Vis initiation kinetics data, displayed in order of increasing k_{init}.

					k_{init} (10^{-4} s^{-1})					
Ru Catalyst	R^1 =	R^2 =	R^3 =	λ_{max}	Trial 1	Trial 2	Trial 3	Average	Std. Dev.	k_{rel}
4	*i*-Pr	H	H	378	0.3835	0.3987	0.4203	0.4008	0.0185	1.00
9	*c*-Pr	H	H	376	0.7198	0.7185	0.7231	0.7205	0.0023	1.80
6	*i*-Pr	H	NO_2	372	0.7514	0.7338	0.7870	0.7574	0.0271	1.89
7	Me	H	H	376	1.478	1.553	1.559	1.530	0.045	3.82
12	1-Ada	H	H	382	3.810	3.289	3.282	3.460	0.303	8.63
10	CH_2*t*-Bu	H	H	374	10.34	11.12	10.96	10.81	0.41	25.7
8	Ph	H	H	370	46.08	49.86	51.43	49.12	2.75	123
11	2-Ada	H	H	380	57.55	52.27	53.36	54.39	2.79	136
5	*i*-Pr	Ph	H	374	85.02	94.26	116.20	98.49	16.02	246

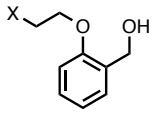
*Synthesis of 2-Cyclopropoxybenzaldehyde (**14**):*

Scheme S1: Overview of synthetic route to 2-cyclopropylbenzaldehyde (**14**).



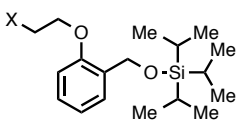


2-(2-chloroethoxy)benzaldehyde (S1) and 2-(2-bromoethoxy)benzaldehyde (S2):[8] To a 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar were added salicylaldehyde (**13**) (3.93 mL, 40.0 mmol), 1-bromo-2-chloroethane (10.0 mL, 120 mmol), cesium carbonate (14.3 g, 44.0 mmol), and DMF (200 mL). The reaction mixture was stirred at 70 °C for 3 h then at 50 °C for 15 h. The flask was allowed to cool to room temperature, and the reaction was quenched with water (200 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with water (100 mL) and brine (2 × 100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography using a gradient solvent system (20:1 hexane:EtOAc → 6:1 hexane:EtOAc) as the eluent provided a mixture of **S1** and **S2** in 4.9:1 molar ratio, as determined by ^{1}H NMR (4.26 g, 55% yield). For simplicity, only analytical data for **S1** are reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.53 (d, J = 0.8 Hz, 1H), 7.85 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.55 (ddd, J_1 = 8.4 Hz, J_2 = 7.3 Hz, J_3 = 1.8 Hz, 1H), 7.09–7.04 (m, 1H), 6.98–6.95 (m, 1H), 4.36 (t, J = 5.7 Hz, 2H), 3.88 (t, J = 5.7 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.66, 160.62, 136.00, 128.63, 125.38, 121.64, 112.79, 68.62, 41.82; **HRMS** (EI+) *m/z* Calcd for $C_9H_9ClO_2$ $[M]^+$ 184.0291, found 184.0338.



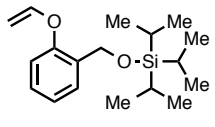
S3 (X = Cl)
S4 (X = Br)

(2-(2-chloroethoxy)phenyl)methanol (S3) and (2-(2-bromoethoxy)phenyl) (S4):[8] To an oven-dried 250 mL round-bottom flask containing a Teflon-coated magnetic stir bar were added a mixture of **S1** and **S2** (4.48 g, 22.1 mmol), THF (50 mL) and MeOH (10 mL). The solution was cooled to 0 °C in an ice bath, and $NaBH_4$ (1.00 g, 26.5 mmol) was added in four portions over 20 min. The reaction mixture was allowed to warm to room temperature and stir for 3 h, before again being cooled to 0 °C. EtOAc (100 mL) and 25% (aq.) NH_4Cl solution (100 mL) were added, and the flask was allowed to warm to room temperature. The phases were separated, and the aqueous phase was further extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with water (100 mL) and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The identify of the product mixture was confirmed by ^{1}H NMR analysis of the crude product, and the material was used in the next step without further purification.



S5 (X = Cl)
S6 (X = Br)

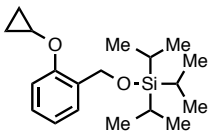
((2-(2-chloroethoxy)benzyl)oxy)triisopropylsilane (S5) and ((2-(2-bromoethoxy)benzyl)oxy)triisopropylsilane (S6):[8] To a 500 mL round-bottom flask containing a Teflon-coated magnetic stir bar, were added DCM (100 mL), the crude mixture of **S3** and **S4** from the previous step (assumed to be 22.1 mmol), and 2,6-lutidine (3.87 mL, 33.2 mmol). The solution was cooled to 0 °C in an ice bath. Triisopropylsilyl triflate (7.71 mL, 28.7 mmol) was added slowly, and the reaction mixture was allowed to warm to room temperature and stir for 18 h, before again being cooled to 0 °C. Saturated $NaHCO_3$ solution (100 mL), 25% (aq.) NH_4OAc solution (100 mL), and Et_2O (150 mL) were added, and the flask was allowed to warm to room temperature. The phases were separated, and the aqueous phase was further extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with water (100 mL) and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography using 25:1 hexane:Et_2O as the eluent provided a mixture of **S5** and **S6** in 4.9:1 molar ratio, as determined by ^{1}H NMR (7.21 g, 93% yield over two steps). For simplicity, only analytical data for **S5** are reported. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.23–7.18 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 4.89 (s, 2H), 4.24 (t, J = 5.9 Hz, 2H), 3.81 (t, J = 5.8 Hz, 2H). 1.25–1.16 (m, 3H), 1.11 (d, J = 7.4 Hz, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.49, 130.97, 127.47, 126.97, 121.48, 110.99, 68.21, 60.19, 42.16, 18.24, 12.21; **HRMS** (FAB+) *m/z* Calcd for $C_{18}H_{31}ClO_2Si$ $[(M+H)–H_2]^+$ 341.1704, found 341.1700.



S8

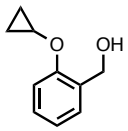
triisopropyl((2-(vinyloxy)benzyl)oxy)silane (S8):[8] To a 250 mL round-bottom flask containing a Teflon-coated magnetic stir bar, were added a mixture of **S5** and **S6** (7.07 g, 20.6 mmol), benzene (100 mL), tetrabutylammonium bisulfate (6.99 g, 20.6 mmol), and a solution of NaOH (8.24 g, 206 mmol) pre-dissolved in H_2O (20 mL). The resulting biphasic reaction mixture was stirred at 65 °C for 48 h. The flask was allowed to cool to room temperature, and 25% (aq.) NH_4OAc solution (10 mL) was added to partition the mixture. The phases were separated, and the aqueous phase was further extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with water (100 mL) and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography using a gradient solvent system (40:1 hexane:Et_2O → 1:1 hexane:Et_2O) as the eluent provided pure **S7** as

a colorless oil (1.17 g, 38% yield) and **S8** containing unknown impurities. A second purification by silica gel column chromatography (40:1 hexane:DCM → 1:1 hexane:DCM) provided pure **S8** as a colorless oil (412 mg, 7% yield). Conversion of **S7** to **S8** using triisopropylsilyl triflate and 2,6-lutidine under analogous conditions to those for the conversion of **S3**/**S4** to **S5**/**S6** provided additional **S8** (1.69 g, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64–7.60 (m, 1H), 7.25–7.20 (m, 1H), 7.13 (td, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 6.92 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 6.61 (dd, J_1 = 13.8 Hz, J_2 = 6.1 Hz, 1H), 4.87 (s, 2H), 4.66 (dd, J_1 = 13.8 Hz, J_2 = 1.7 Hz, 1H), 4.39 (dd, J_1 = 6.1 Hz, J_2 = 1.7 Hz, 1H), 1.24–1.15 (m, 3H), 1.10 (d, J = 6.9 Hz, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.89, 148.71, 131.96, 127.68, 127.29, 123.60, 116.10, 94.50, 60.11, 18.23, 12.20; **HRMS** (FAB+) *m/z* Calcd for $C_{18}H_{28}O_2Si$ $[(M+H)–H_2]^+$ 305.1937, found 305.1934.



S9

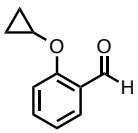
((2-cyclopropoxybenzyl)oxy)triisopropylsilane (S9):[8] To an oven-dried 100 mL round-bottom flask containing a Teflon-coated magnetic stir bar under an Ar atmosphere, were added triisopropyl((2-(vinyloxy)benzyl)oxy)silane (**S8**) (2.10 g, 6.85 mmol), DCM (50 mL), and chloroiodomethane (3.0 mL, 41.1 mmol). The solution was cooled to 0 °C in an ice bath, and diethylzinc solution (1.0 M in hexane) was added dropwise over 30 min. *(CAUTION: Diethylzinc is highly pyrophoric and should only be handled under inert atmosphere in a well-maintained fumehood. The operator should have appropriate protection at all times.)* The reaction was allowed to stir at 0 °C for an additional 15 min, then at room temperature for 2.5 h. During this time, a white precipitate was observed. The solution was again cooled to 0 °C, and MeOH (1 mL), H_2O (1 mL), and 6.0 N HCl solution (1 mL) were carefully added in succession. The mixture was transferred to a separatory funnel, and Et_2O (50 mL) and H_2O (50 mL) were added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (40:1 hexanes:Et_2O → 20:1 hexanes:Et_2O) to give **S9** as a colorless oil (2.02 g, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58–7.53 (m, 1H), 7.25–7.16 (m, 2H), 7.03–6.97 (m, 1H), 4.77 (s, 2H), 3.75–3.71 (m, 1H), 1.25–1.14 (m, 3H), 1.10 (d, J = 7.0 Hz, 18H), 0.82–0.70 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.29, 130.06, 127.31, 126.59, 120.82, 111.68, 60.21, 50.71, 18.24, 12.22, 6.47; **HRMS** (EI+) *m/z* Calcd for $C_{19}H_{31}O_2Si$ $[(M+H)–H_2]^+$ 319.2093, found 319.2105.



S10

(2-cyclopropoxyphenyl)methanol (S10):[8] To an oven-dried 100 mL round-bottom flask containing a Teflon-coated magnetic stir bar under an Ar atmosphere, were added ((2-cyclopropoxybenzyl)oxy)triisopropylsilane (**S9**) (2.02 g, 6.30 mmol) and THF (20 mL). TBAF (1.0 M in THF) solution (7.6 mL, 7.6 mmol) was added, and the solution was allowed to stir at room temperature for 90 min. The reaction was quenched with 25% NH_4OAc solution (50 mL) and was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (2:1 hexanes:EtOAc) to give **S10** as a colorless oil (898 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.22 (m, 3H), 6.96 (td, J_1 = 7.2 Hz, J_2 = 1.4 Hz, 1H), 4.63 (d, J = 6.5 Hz, 2H), 3.84–3.71 (m, 1H), 2.24 (t, J = 6.6 Hz, 1H), 0.88–0.66 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ

156.96, 129.04, 128.95, 128.78, 121.09, 112.55, 62.22, 51.02, 6.55; **HRMS** (FAB+) *m/z* Calcd for $C_{10}H_{12}O_2$ $[M]^+$ 164.0837, found 164.0837.



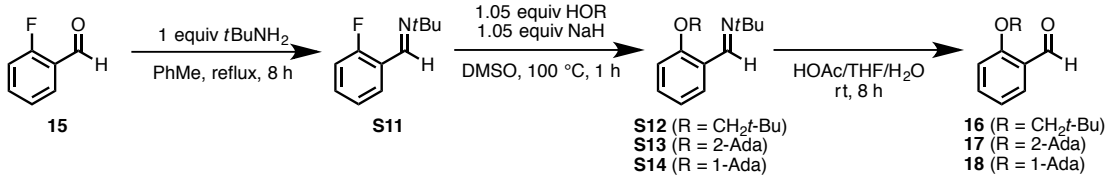
14

2-cyclopropoxybenzaldehyde (14):[9] To a 250 mL round-bottom flask containing a Teflon-coated magnetic stir bar, were added (2-cyclopropoxyphenyl)methanol (**S10**) (899 mg, 5.44 mmol) and DCM (50 mL). PCC (2.35 g, 10.88 mmol) was added in a single portion. *(CAUTION: PCC is an extremely toxic chemical and should be handled in a well-maintained fumehood. The operator should have appropriate protection at all times. Excess PCC and the reduced chromium salt byproducts should be collected in a separate waste stream and safely disposed.)* The solution quickly changed color from orange to brown. The reaction was allowed to stir at room temperature for 1 h. The solution was filtered through a pad of Celite, which was subsequently washed with EtOAc (5 × 20 mL). The filtrate was concentrated *in vacuo*. The resulting dark brown residue was purified by silica gel column chromatography (40:1 hexanes:EtOAc → 10:1 hexanes:EtOAc) to provide **14** as a pale yellow oil (693 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.40 (d, J = 0.8 Hz, 1H), 7.82 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H), 7.56 (ddd, J_1 = 8.4 Hz, J_2 = 7.3 Hz, J_3 = 1.8 Hz, 1H), 7.36 (dd, J_1 = 8.4 Hz, J_2 = 0.7 Hz, 1H), 7.11–6.95 (m, 1H), 3.89–3.80 (m, 1H), 0.90–0.77 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.84, 161.51, 135.89, 128.34, 124.82, 121.09, 113.89, 51.55, 6.49; **HRMS** (EI+) *m/z* Calcd for $C_{10}H_{10}O_2$ $[M]^+$ 162.0681, found 162.0715.

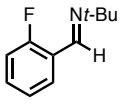
General Three-Step S_NAr Procedure:

Our group recently disclosed a three-step synthesis of sterically hindered *ortho*-alkoxybenzaldehydes via S_NAr chemisty.[10] Included in that manuscript were syntheses of compounds **16**–**18**. We have reproduced that procedure, including details specific to compounds **16**–**18**, here for convenience.

Scheme S2: General depiction of three-step S_NAr route for synthesizing 2-alkoxybenzaldehydes.



15 **S11** **S12** (R = CH_2*t*-Bu) **S13** (R = 2-Ada) **S14** (R = 1-Ada) **16** (R = CH_2*t*-Bu) **17** (R = 2-Ada) **18** (R = 1-Ada)



S1

***N-tert*-butyl-1-(2-fluorophenyl)methanimine (S11):**[10,11] To a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar were added *tert*-butylamine (1.04 mL, 10.0 mmol), 2-fluorobenzaldehyde (**15**) (1.05 mL, 10.0 mmol), and toluene (50 mL). The flask was equipped with a Dean–Stark apparatus wrapped in aluminum foil and a reflux condenser. The reaction was allowed to stir at vigorous reflux (140–150 °C) for 8 h. During the course of the reaction, water accumulated at the bottom of the Dean–Stark apparatus. The reaction was allowed to cool to room temperature. A small aliquot was taken, concentrated *in vacuo*, and analyzed by ^{1}H NMR to monitor reaction progress. (2-Fluorobenzaldehyde (**15**) has a characteristic ^{1}H NMR peak at 10.35 ppm (s, 1H) in $CDCl_3$, and the product (**S11**) has a ^{1}H NMR peak at 8.57 ppm (s, 1H); comparison of these two peaks provides a convenient means of monitoring reaction progress.) In cases where the reaction had

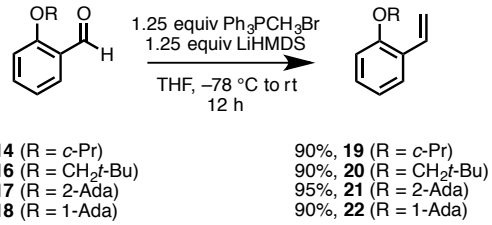
not proceeded to >95% conversion, an additional portion of *tert*-butylamine commensurate with the amount of starting material remaining was added, and the reaction was heated for an additional 2–4 h. Upon completion, the reaction mixture was allowed to cool to room temperature, and the solvent was removed *in vacuo*. The crude imine product (**S11**) was obtained as a yellow oil and was used in the subsequent step without further purification. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.00 (td, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.41–7.31 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.10–7.02 (m, 1H), 1.30 (s, 9H).

General S_NAr Procedure (S12–S14):[10,12] To a 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar under Ar, were added dry NaH (252 mg, 10.5 mmol), DMSO (20 mL), and the appropriate alcohol (10.0 mmol). Upon addition of the alcohol, vigorous bubbling was observed. The solution was allowed to stir at room temperature, at which point it became a white suspension. A solution of crude *N*-*tert*-butyl-1-(2-fluorophenyl)methanimine (**S11**) (assumed to be 10.0 mmol) in DMSO (10 mL) was added. The reaction mixture was heated to 100 °C for 1 h, during which time it changed color from yellow to red to brown. After 1 h, a small aliquot of the reaction mixture was removed with a syringe and quenched with H_2O. The resulting mixture was extracted with Et_2O, and the organic phase was concentrated *in vacuo* and examined by ^{1}H NMR spectroscopy to monitor reaction progress. (**S11** has a characteristic ^{1}H NMR peak at 8.57 ppm (s, 1H) in $CDCl_3$, and the product has a ^{1}H NMR peak at 8.78 ppm (s, 1H) for **S12**, 8.77 ppm (s, 1H) for **S13**, and 8.74 ppm (s, 1H) for **S14**; comparison of these peaks provides a convenient means of monitoring reaction progress.) In instances where the reaction had not proceeded to completion (*i.e.*, >95% conversion) an additional portion of NaH and alcohol commensurate with the amount of starting material remaining was added, and the reaction mixture was heated at 100 °C for an additional 1 h. Upon completion of the reaction, the flask was allowed to cool to room temperature. The reaction mixture was carefully poured into a separatory funnel containing 100 mL of H_2O to quench residual base. The mixture was extracted with Et_2O (3 × 100 mL). The organic layers were combined and concentrated *in vacuo*. The crude product was obtained as a pink oil or off-white solid and was used in the next step without further purification.

General Acidic Hydrolysis Procedure (16–18):[10,12] To a 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar, were added crude **S12**, **S13**, or **S14** (assumed to be 10.0 mmol). A 50:15:1 H_2O:THF:HOAc solution (132 mL) was added, and the reaction was stirred at room temperature for 8 h. THF was removed *in vacuo*, and the resulting aqueous solution was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel column chromatography using a gradient solvent system (100:1 hexane:Et_2O → 40:1 hexane:Et_2O) as the eluent, gave the product as a white or off-white solid. The final yield was calculated for the combined three steps.

General Wittig Olefination Procedure:

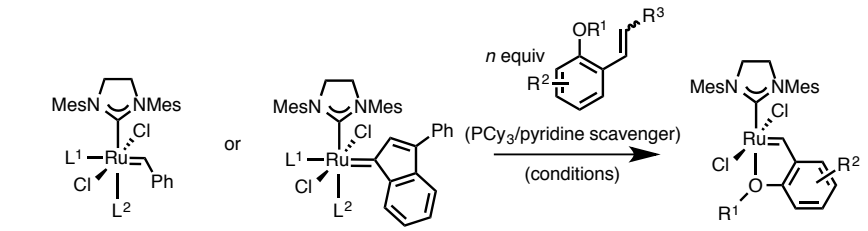
Scheme S3: General depiction of Wittig olefination reaction.



General Wittig Olefination Procedure (19–22):[10,13] To a flame-dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar under Ar, were added methyltriphenylphosphonium bromide (1.34 g, 3.75 mmol) and anhydrous THF (20 mL). LiHMDS solution (1.0 M in THF) (3.75 mL, 3.75 mmol) was added at 0 °C. The resulting yellow solution was allowed to warm to room temperature are stir until it became homogeneous (approximately 1 h). The solution was cooled to –78 °C in a dry ice/acetone bath, and the appropriate 2-alkoxybenzaldehyde (**14** or **16–18**) was added (3.0 mmol). The solution was allowed to warm to room temperature are stir overnight (approximately 12 h). Et_2O (30 mL) was added, and the resulting heterogeneous solution was cooled to –20 °C for 30 min. The solution was filtered through a pad of Celite to remove the triphenylphosphine oxide precipitate, and the Celite was washed twice with Et_2O that had been cooled to 0 °C. The filtrate was concentrated *in vacuo*, and the resulting yellow oil was purified by silica gel column chromatography using a gradient solvent system (100:1 hexane:Et_2O → 40:1 hexane:Et_2O) as the eluent. The pure product was thus obtained as a white solid or colorless oil. To prevent polymerization during prolonged storage, all styrenes were kept under an Ar atmosphere at –20 °C.

Styrene Chelation:

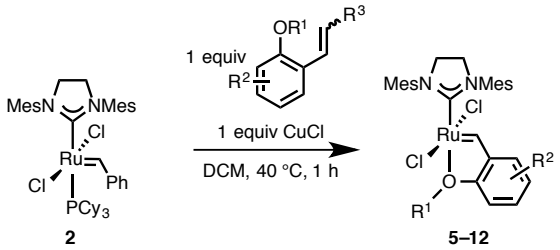
Scheme S4: General depiction of styrene chelation reactions.



Procedure for Optimization/Evaluation of Chelation Conditions:[14–16] To a flame-dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar under Ar, were added catalysts **2**, **23**,[17] or **S15–S17**[18–20] (0.2 mmol), phosphine/pyridine scavenger, styrene, and solvent (5 mL). The reaction was stirred at the appropriate temperature for the indicated duration, during which time a color change from maroon to brown or green was observed. The reaction vessel was allowed to cool to room temperature. When Amberlyst-15 resin was used as the

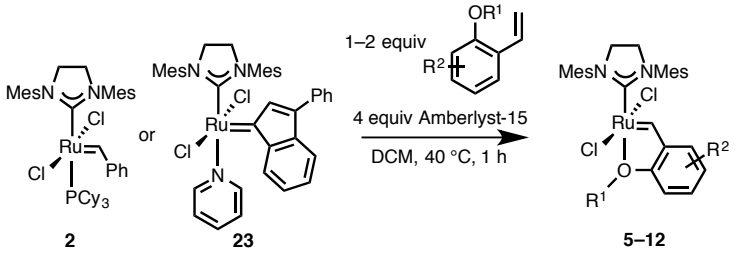
phosphine/pyridine scavenger,[15,16] the reaction mixture was filtered through a pad of cotton in a glass pipette to remove the Amberlyst-15 resin. The resulting filtrate was concentrated *in vacuo* to give a brown residue. Pentane (10 mL) was added, and the resulting suspension was sonicated for 1 min, during which time the pentane phase became dark brown, and a green precipitate was observed. The suspension was filtered through a fritted Buchner filter funnel. The green precipitate was washed sequentially with methanol (2 × 5 mL) and pentane (2 × 5 mL) and then dried under high vacuum to give the analytically pure product as a green solid. When CuCl was used as the phosphine scavenger,[14] the volatiles were removed *in vacuo* to give a green or brown residue. The crude product was dissolved in a minimal amount of 1:1 hexane:DCM, at which point a white precipitate, CuCl•PCy_3, was observed. The suspension was filtered through a pad of cotton in a glass pipette to remove CuCl•PCy_3, and the solution was loaded directly onto a silica gel column. The column was performed first using 4:1 hexane:Et_2O as the eluent to remove organic byproducts. Next, DCM was used as the eluent, at which point the product eluted rapidly. The fractions containing the product were combined, concentrated *in vacuo*, and dried under high vacuum to give the analytically pure product as a green microcrystalline solid. The results are shown in Tables S2–S9.

Scheme S5: General depiction of styrene chelation reaction using the CuCl procedure.



General Chelation Procedure with CuCl (Method A):[14] To a flame-dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar under Ar, were added Grubbs 2nd generation catalyst (**2**) (170 mg, 0.2 mmol), CuCl (19.8 mg, 0.2 mmol), the appropriate styrene (0.2 mmol) and DCM (5 mL). The reaction was stirred at 40 °C for 1 h, during which time a color change from maroon to brown or green was observed. The reaction vessel was allowed to cool to room temperature, and the volatiles were removed *in vacuo* to give a green or brown residue. The crude product was dissolved in a minimal amount of 1:1 hexane:DCM, at which point a white precipitate, CuCl•PCy_3, was observed. The suspension was filtered through a pad of cotton in a glass pipette to remove CuCl•PCy_3, and the solution was loaded directly onto a silica gel column. The column was performed first using 4:1 hexane:Et_2O as the eluent to remove organic byproducts. Next, DCM was used as the eluent, at which point the product eluted rapidly. The fractions containing the product were combined, concentrated *in vacuo*, and dried under high vacuum to give the analytically pure product as a green microcrystalline solid.

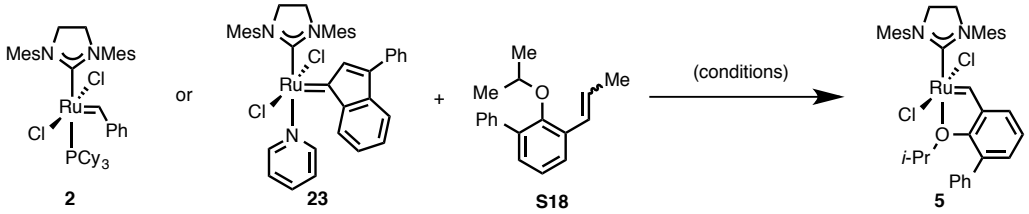
Scheme S6: General depiction of styrene chelation reaction using the Amberlyst-15 procedure.



General Chelation Procedure with Amberlyst-15 Resin (Methods B and C):[15,16] To a flame-dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar under Ar, were added Grubbs 2nd generation catalyst (**2**) (170 mg, 0.2 mmol) or Umicore M31 (**23**) (149 mg, 0.2 mmol), dry Amberlyst-15 hydrogen form (4.7 mmol H^+/g) (170 mg, 0.8 mmol H^+), the appropriate styrene (0.2 or 0.4 mmol) and DCM (5 mL). The reaction was stirred at 40 °C for 1 h, during which time a color change from maroon to brown or green was observed. The reaction vessel was allowed to cool to room temperature, and the reaction mixture was filtered through a pad of cotton in a glass pipette to remove the Amberlyst-15 resin. The resulting filtrate was concentrated *in vacuo* to give a brown residue. Pentane (10 mL) was added, and the resulting suspension was sonicated for 1 min, during which time the pentane phase became dark brown, and a green precipitate was observed. The suspension was filtered through a fritted Buchner filter funnel. The green precipitate was washed sequentially with methanol (2 × 5 mL) and pentane (2 × 5 mL) and then dried under high vacuum to give the analytically pure product as a green solid.

Catalyst **S17**[20] was found to give comparable yields to **23** in many cases under conditions otherwise identical to Method C. These two catalysts differ only by the presence of an additional pyridine group in **S17**. It is unknown whether the additional pyridine is a true inner-sphere ligand on the ruthenium center (as drawn) or is merely trapped in the solid-state (micro)crystalline lattice. For the purposes of this project, large quantities of **S17** were donated by Materia, Inc., which is why it was used in many cases. Researchers who desire to prepare catalysts **5**–**12** may wish either to purchase **23** (available from Aldrich) or to prepare **23**[17] or **S17**[20] following known literature procedure, depending on which option is more convenient.

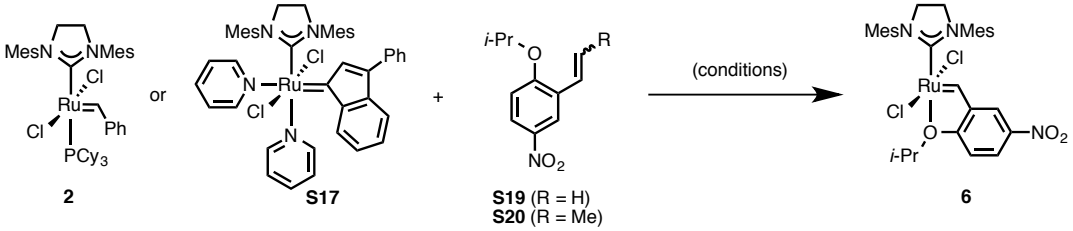
Table S2: Synthesis of catalyst **5** under different reaction conditions.



Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**S18**)	Temp.	Time	Yield
1[a]	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	34%
2	**2**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	0%
3	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	43%

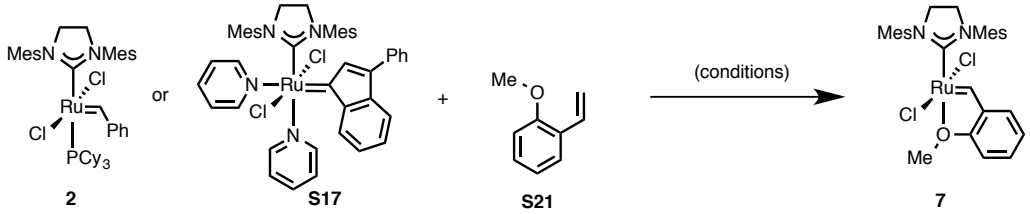
[a] All manipulations were carried out in a glovebox; 0.1 mmol scale.

Table S3: Synthesis of catalyst **6** under different reaction conditions.



Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv (**S19**)	40 °C	1 h	24%
2	**2**	A	1 equiv CuCl	DCM	1 equiv (**S20**)	40 °C	1 h	20%
3	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv (**S20**)	40 °C	1 h	0%
4	**S17**	---	4 equiv Amberlyst-15	DCM	1 equiv (**S20**)	40 °C	1 h	55%

Table S4: Synthesis of catalyst **7** under different reaction conditions.

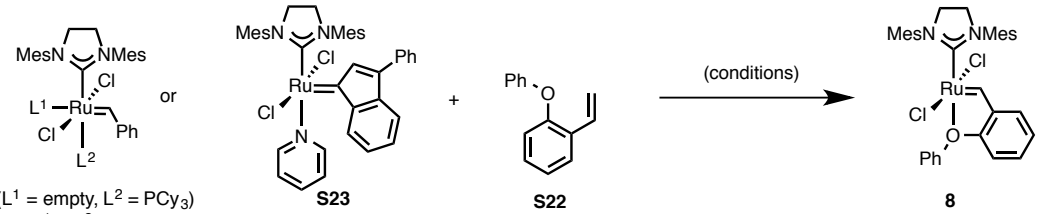


2 **S17** **S21** **7**

Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**S21**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	58%
2	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	18%
3[a]	**S17**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	50–54%

[a] 0.4-mmol scale.

Table S5: Synthesis of catalyst **8** under different reaction conditions.

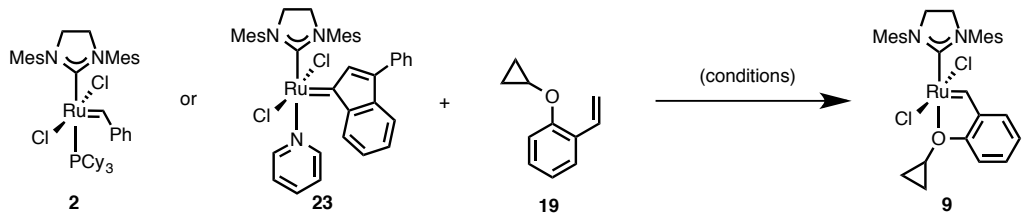


2 (L^1 = empty, L^2 = PCy_3)
S15 (L^1 = L^2 = pyridine)

S23 **S22** **8**

Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**S22**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	0–14%
2	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	0–14%
3	**S15**	---	4 equiv Amberlyst-15	DCM	1.5 equiv	40 °C	1 h	0%
4	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	40%

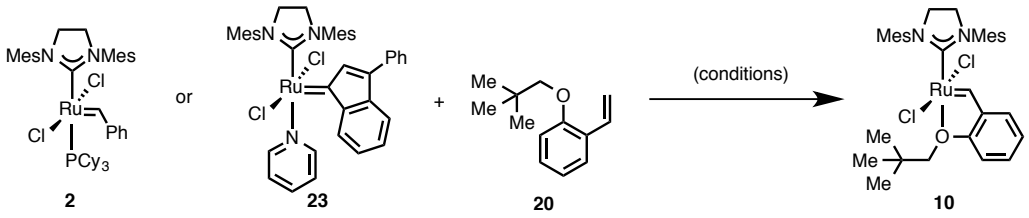
Table S6: Synthesis of catalyst **9** under different reaction conditions.



2 **23** **19** **9**

Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**19**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	80%
2	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	51%
3	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	75%

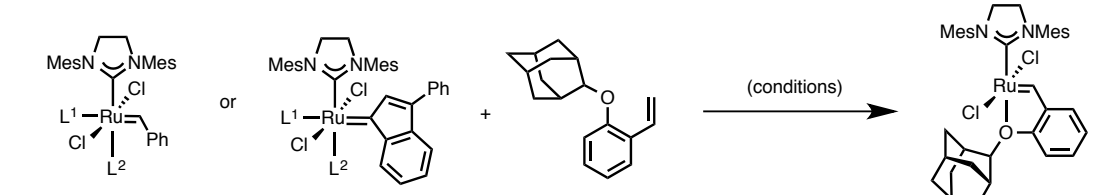
Table S7: Synthesis of catalyst **10** under different reaction conditions.



2 **23** **20** **10**

Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**19**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	43%
2	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	15%
3	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	79%

Table S8: Synthesis of catalyst **11** under different reaction conditions.



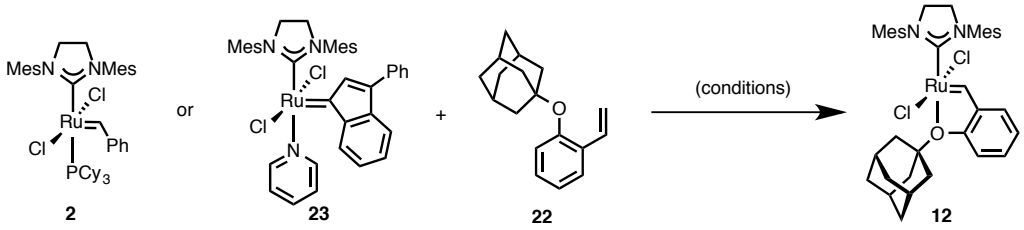
2 (L^1 = empty, L^2 = PCy_3)
S15 (L^1 = L^2 = pyridine)

S16 (L^1 = empty, L^2 = PCy_3)
S17 (L^1 = L^2 = pyridine)
23 (L^1 = empty, L^2 = pyridine)

21 **11**

Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**21**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	10–34%
2	**2**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	24–25%
3	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	38%
4	**2**	---	4 equiv Amberlyst-15	THF	1 equiv	40 °C	1 h	13%
5	**2**	---	4 equiv Amberlyst-15	PhMe	1equiv	40 °C	1 h	10%
6	**2**	---	4 equiv Amberlyst-15	PhMe	1 equiv	40 °C	10 h	16%
7	**S15**	---	8 equiv Amberlyst-15	DCM	1 equiv	rt	1 h	28%
8	**S16**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	0%
9	**S17**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	61%
10	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	74%
11	**23**	---	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	64%

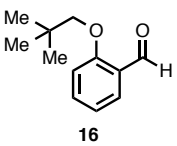
Table S9: Synthesis of catalyst **12** under different reaction conditions.



Entry	Starting Catalyst	Method	PCy_3/Pyridine Scavenger	Solvent	Styrene (**22**)	Temp.	Time	Yield
1	**2**	A	1 equiv CuCl	DCM	1 equiv	40 °C	1 h	57–64%
2	**2**	---	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	33%
3	**2**	B	4 equiv Amberlyst-15	DCM	2 equiv	40 °C	1 h	35%
4	**23**	C	4 equiv Amberlyst-15	DCM	1 equiv	40 °C	1 h	79%

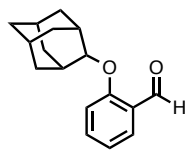
Characterization of New Compounds:

The analytical data for *ortho*-alkoxybenzaldehyes **16**–**18** have been previously reported by our group.[10] The data (including NMR spectra) are reproduced here for convenience.



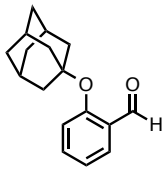
16

2-(neopentyloxy)benzaldehyde (16): The title compound was prepared from 2-fluorobenzaldehyde (1.05 mL, 10.0 mmol) and neopentyl alcohol (926 mg, 10.5 mmol) according to the general three-step S_NAr procedure. Purification by silica gel column chromatography (40:1 hexane:Et_2O → 20:1 hexane:Et_2O) provided the product as a colorless oil (1.46 g, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.59 (d, J = 0.8 Hz, 1H), 7.84 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.53 (ddd, J_1 = 8.4 Hz, J_2 = 7.3 Hz, J_3 = 1.9 Hz, 1H), 7.03–6.99 (m, 1H), 6.98–6.95 (m, 1H), 3.72 (s, 2H), 1.08 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.7, 162.0, 136.0, 128.3, 125.2, 120.6, 112.6, 78.5, 32.3, 26.8; **HRMS** (FAB+) *m/z* Calcd for $C_{12}H_{17}O_2$ $[M+H]^+$ 193.1229, found 193.1252.



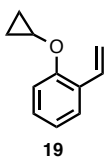
17

2-(((1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl)oxy)benzaldehyde (17): The title compound was prepared from 2-fluorobenzaldehyde (1.05 mL, 10.0 mmol) and 2-adamantanol (1.59 g, 10.5 mmol) according to the general three-step S_NAr procedure. Purification by silica gel column chromatography (20:1 hexane:Et_2O → 10:1 hexane:Et_2O) provided the product as a white solid (1.01 g, 40% yield). **mp** = 69–71 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.63 (d, J = 0.8 Hz, 1H), 7.84 (dd, J_1 = 7.9 Hz, J_2 = 1.9 Hz, 1H), 7.49 (ddd, J_1 = 8.5 Hz, J_2 = 7.3 Hz, J_3 = 1.9 Hz, 1H), 6.99–6.95 (m, 2H), 4.58 (t, J = 3.2 Hz, 1H), 2.25–2.19 (m, 2H), 2.16–2.10 (m, 2H), 1.97–1.86 (m, 4H), 1.83–1.75 (m, 4H), 1.62–1.57 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.18, 160.43, 135.85, 128.50, 125.85, 120.35, 114.00, 80.20, 37.42, 36.42, 31.77, 31.67, 27.26, 27.18; **HRMS** (EI+) *m/z* Calcd for $C_{17}H_{20}O_2$ $[M]^+$ 256.1463, found 256.1453.



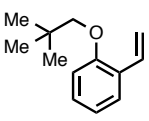
18

2-(((1*s*,3*s*)-adamantan-1-yl)oxy)benzaldehyde (18): The title compound was prepared from 2-fluorobenzaldehyde (1.05 mL, 10.0 mmol) and 1-adamantanol (1.59 g, 10.5 mmol) according to the general three-step S_NAr procedure. Purification by silica gel column chromatography (40:1 hexane:Et_2O) provided the product as an off-white solid (609 mg, 24% yield). **mp** = 90–93 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.49 (d, J = 0.8 Hz, 1H), 7.84 (dd, J_1 = 7.7 Hz, J_2 =1.9 Hz, 1H), 7.50 (ddd, J_1 = 8.2 Hz, J_2 = 7.3 Hz, J_3 = 1.9 Hz, 1H), 7.18–7.12 (m, 2H), 2.23–2.18 (m, 3H), 1.96–1.91 (m, 3H), 1.69–1.58 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.24, 158.24, 134.87, 131.20, 127.92, 125.13, 123.60, 80.57, 43.05, 36.10, 31.11; **HRMS** (FAB+) *m/z* Calcd for $C_{17}H_{19}O_2$ $[(M+H)–H_2]^+$ 255.1385, found 255.1376.



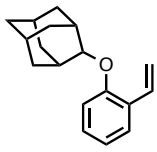
19

1-cyclopropoxy-2-vinylbenzene (19): The title compound was prepared from from 2-cyclopropoxybenzaldehyde **(14)** (487 mg, 3.00 mmol) according to the general Wittig procedure and was obtained as a pale yellow oil (431 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49–7.43 (m, 1H), 7.26–7.23 (m, 2H), 7.03–6.90 (m, 2H), 5.72 (dd, J_1 = 17.8 Hz, J_2 = 1.5 Hz, 1H), 5.24 (dd, J_1 = 11.2 Hz, J_2 = 1.5 Hz, 1H), 3.78–3.73 (m, 1H), 0.82–0.76 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.23, 131.69, 128.80, 126.63, 126.51, 120.96, 114.49, 113.07, 51.04, 6.45; **HRMS** (EI+) *m/z* Calcd for $C_{11}H_{12}O$ $[M]^+$ 160.0888, found 160.0931.



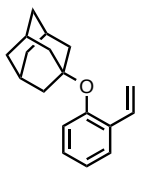
20

1-(neopentyloxy)-2-vinylbenzene (20): The title compound was prepared from 2-(neopentyloxy)benzaldehyde (**16**) (577 mg, 3.00 mmol) according to the general Wittig procedure and was obtained as a colorless oil (511 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (dd, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 7.21 (ddd, J_1 = 8.2 Hz, J_2 = 7.4 Hz, J_3 = 1.7 Hz, 1H), 7.12 (dd, J_1 = 17.8 Hz, J_2 = 11.2 Hz, 1H), 6.94–6.89 (m, 1H), 6.84 (dd, J_1 = 8.2 Hz, J_2 = 0.8 Hz, 1H), 5.76 (dd, J_1 = 17.8 Hz, J_2 = 1.6 Hz, 1H), 5.25 (dd, J_1 = 11.2 Hz, J_2 = 1.5 Hz, 1H), 3.63 (s, 2H), 1.07 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.65, 131.86, 128.93, 127.05, 126.46, 120.50, 114.13, 111.99, 78.37, 32.24, 26.93; **HRMS** (EI+) *m/z* Calcd for $C_{13}H_{18}O$ $[M]^+$ 190.1358, found 190.1317.



21

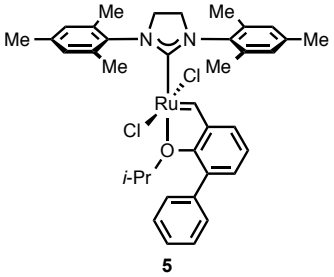
(1*r*,3*r*,5*r*,7*r*)-2-(2-vinylphenoxy)adamantane (21): The title compound was prepared from 2-(((1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl)oxy)benzaldehyde (**17**) (769 mg, 3.00 mmol) according to the general Wittig procedure and was obtained as a white solid (727 mg, 95% yield). **mp** = 89–91 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 7.22–7.16 (m, 2H), 6.91–6.87 (m, 1H), 6.86 (d, J = 8.3 Hz, 1H), 5.75 (dd, J_1 = 17.8 Hz, J_2 = 1.6 Hz, 1H), 5.25 (dd, J_1 = 11.1 Hz, J_2 = 1.5 Hz, 1H), 4.47 (t, J = 3.0 Hz, 1H), 2.22–2.16 (m, 4H), 1.94–1.85 (m, 4H), 1.78 (d, J = 13.8 Hz, 4H), 1.60–1.54 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.78, 131.99, 128.74, 127.81, 126.52, 120.34, 113.89, 113.60, 79.72, 37.65, 36.57, 31.89, 31.74, 27.47, 27.39; **HRMS** (EI+) *m/z* Calcd for $C_{18}H_{22}O$ $[M]^+$ 254.1671, found 254.1681.



22

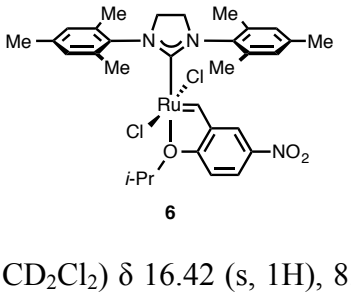
(1*s*,3*s*)-1-(2-vinylphenoxy)adamantane (22): The title compound was prepared from 2-(((1*s*,3*s*)-adamantan-1-yl)oxy)benzaldehyde (**18**) (513 mg, 2.00 mmol) according to the general Wittig procedure and was obtained as a pale yellow oil (456 mg, 90% yield). **mp** = 39–41 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.20–7.14 (m, 2H), 7.08–7.02 (m, 2H), 5.70 (dd, J_1 = 17.9 Hz, J_2 =1.4 Hz, 1H), 5.23 (dd, J_1 = 11.1 Hz, J_2 = 1.4 Hz, 1H), 2.19–2.15 (m, 3H), 1.94–1.90 (m, 6H), 1.66–1.57 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.43, 133.12, 128.00, 125.65, 124.92, 123.51, 113.49, 79.51, 43.11, 36.28, 31.11; **HRMS** (EI+) *m/z* Calcd for $C_{18}H_{22}O$ $[M]^+$ 254.1671, found 254.1676.

In the NMR spectra for the catalyst below, several hydrogen and carbon atoms that would typically appear as single resonances in Hoveyda-type catalysts actually give pairs of resonances, which in some cases are broad. This suggests that rotation about the C(SIMes)–Ru bond may be slow at room temperature on the NMR time scale, and that two distinct populations of catalyst conformations are present in solution. In the peak listings below, tentative assignments of relevant peaks are included for clarity.



5

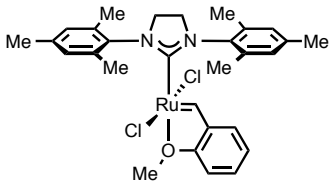
Blechert catalyst (5): The title compound was prepared on a 0.2 mmol scale from (*E*/*Z*)-2-isopropoxy-3-(prop-1-en-1-yl)-1,1'-biphenyl (**S18**)[21] (50 mg, 0.2 mmol) using Method C, and it was obtained as a green microcrystalline solid (60 mg, 43% yield). Analytical data were in agreement with published data.[3] In our hands, it was found that the title compound decomposed rapidly in solution in solvents that were not rigorously dried and degassed. Thus, when using Method A, all manipulations were performed in the glovebox. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.62 (s, 1H), 7.41–7.30 (m, 6H), 7.07 (bs, 4H), 6.99 (t, J = 7.5 Hz, 1H), 6.92 (dd, J_1 = 7.5 Hz, J_2 = 1.7 Hz, 1H), 4.35 (sept, J = 6.3 Hz, 1H), 4.16 (s, 4H), 2.45 (bs, 18H), 0.80 (d, J = 6.3 Hz, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 298.17, 210.63, 149.29, 148.53, 140.24 (bs, *C*(Mes)–N), 139.72, 139.32, 138.80 (bs, *C*(Mes)–N), 134.63 (bs), 133.64, 131.93, 129.72 (bs), 129.46, 128.91, 128.19, 123.96, 121.77, 77.91, 51.94 (bs), 21.38, 20.53, 18.65 (bs); **X-ray** (single-crystal) Green block crystals of X-ray diffraction quality were obtained by allowing a saturated solution of **5** in pentane to stand unperturbed at –20 °C for several days (CCDC 1017843).[22]



6

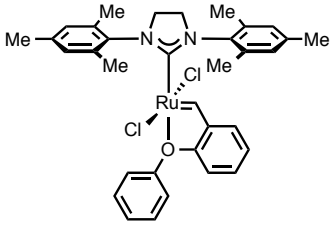
Grela catalyst (6): The title compound was prepared on a 0.2 mmol scale from (*E*/*Z*)-1-isopropoxy-4-nitro-2-(prop-1-en-1-yl)benzene (**S20**)[21] (44 mg, 0.2 mmol) and **S17** (168 mg, 0.2 mmol) following a procedure otherwise identical to Method C. Catalyst **6** was obtained as a green microcrystalline solid (74 mg, 55% yield). 1-Isopropoxy-4-nitro-2-vinylbenzene (**S19**)[23] was equally effective. Analytical data were in agreement with published data.[24] **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.42 (s, 1H), 8.44 (dd, J_1 = 9.0 Hz, J_2 = 2.7 Hz, 1H), 7.81 (d, J = 2.7 Hz, 1H), 7.10 (s, 4H), 6.94 (d, J = 9.0 Hz, 1H), 4.98 (sept, J = 6.1 Hz, 1H), 4.19 (s, 4H), 2.44 (s, 18H), 1.27 (d,

J = 6.1 Hz, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 290.42 (Ru=*C*HAr), 290.31 (Ru=*C*HAr), 208.38, 156.78, 145.07, 143.65, 139.77, 139.50, 136.29, 129.91, 124.64, 117.33, 113.43, 78.34, 52.11, 21.35, 19.64.



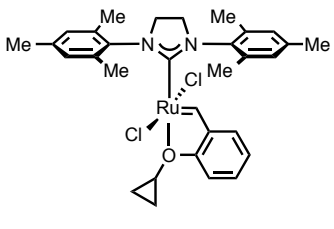
7

methoxy catalyst (7): The title compound was prepared on a 0.4 mmol scale from 2-vinylanisole (**S21**) (54 mg, 0.4 mmol) and **S17** (337 mg, 0.4 mmol) following a procedure otherwise identical to Method C. Catalyst **7** was obtained as a green microcrystalline solid (120–129 mg, 50–54% yield). Analytical data were in agreement with published data.[25] **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.48 (s, 0.5H, Ru=C*H*Ar), 16.48 (s, 0.5H, Ru=C*H*Ar), 7.61–7.55 (m, 1H), 7.09 (bs, 4H), 6.97–6.95 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 12H), 2.43 (s, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 290.49 (Ru=*C*HAr), 290.38 (Ru=*C*HAr), 210.48, 154.16, 144.55, 139.38, 139.17, 136.85, 130.12, 129.93, 123.90, 122.10, 112.12, 58.83, 52.30, 21.46, 19.54; **HRMS** (FAB+) *m/z* Calcd for $C_{29}H_{35}Cl_2N_2ORu$ $[M]^+$ 598.1092, found 598.1071.



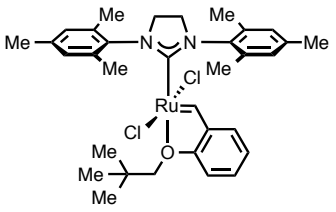
8

Plenio catalyst (8): The title compound was prepared on a 0.2 mmol scale from 1-phenoxy-2-vinylbenzene (**S22**)[16] (39 mg, 0.2 mmol) using Method C, and it was obtained as a green microcrystalline solid (53 mg, 40% yield). Analytical data were in agreement with published data.[16] **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.66 (s, 0.5H, Ru=C*H*Ar), 16.65 (s, 0.5H, Ru=C*H*Ar), 7.49–7.44 (m, 1H), 7.32–7.27 (m, 2H), 7.26–7.21 (m, 1H), 7.20–7.17 (m, 2H), 7.07–7.03 (m, 5H), 7.03–6.99 (m, 1H), 6.68 (d, J = 8.3 Hz, 1H), 4.14 (s, 4H), 2.43 (s, 12H), 2.39 (s, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 290.76–290.62 (Ru=*C*HAr), 209.34, 153.65, 152.98, 144.37, 139.38, 139.15, 136.60, 129.88, 129.83, 129.79, 126.59, 124.80, 122.75, 122.29, 114.59, 52.27, 21.38, 19.54.



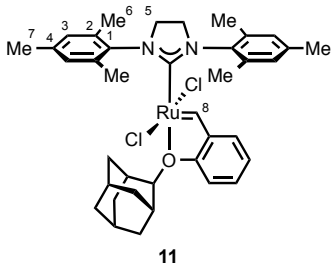
9

cyclopropoxy catalyst (9): The title compound was prepared on a 0.2 mmol scale from **19** (32 mg, 0.2 mmol) using Method C, and it was obtained as a green microcrystalline solid (94 mg, 75% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.50 (s, 1H), 7.66–7.52 (m, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.10 (bs, 4H), 7.01–6.93 (m, 2H), 4.16 (s, 4H), 3.89 (tt, J_1 = 6.1 Hz, J_2 = 2.9 Hz, 1H), 2.44 (s, 18H), 0.89–0.75 (m, 2H), 0.68–0.53 (m, 2H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 293.03 (bs), 211.45, 154.14, 145.04, 139.60 (bs), 139.52, 136.69, 129.95, 129.93, 124.17, 122.16, 113.79, 55.69, 52.26, 21.47, 19.74 (bs), 6.45; **HRMS** (FAB+) *m/z* Calcd for $C_{31}H_{36}Cl_2N_2ORu$ $[M]^+$ 624.1249, found 624.1234; **X-ray** (single-crystal) Green block crystals of X-ray diffraction quality were obtained by carefully layering pentane onto a 0.01 M solution of **9** in C_6D_6 and allowing the biphasic mixture to stand at room temperature overnight (CCDC 1044211).[22]



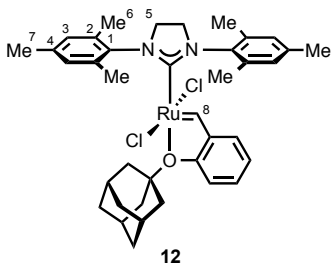
10

neopentyloxy catalyst (10): The title compound was prepared on a 0.2 mmol scale from **20** (38 mg, 0.2 mmol) using Method C and obtained as a green microcrystalline solid (103 mg, 79% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.58 (s, 1H), 7.54 (ddd, J_1 = 8.7 Hz, J_2 = 7.2 Hz, J_3 = 1.9 Hz, 1H), 7.06 (bs, 4H), 6.98–6.89 (m, 3H), 4.14 (s, 4H), 4.08 (s, 2H), 2.45 (s, 12H), 2.41 (s, 6H), 0.87 (s, 9H); **^{13}C NMR** (500 MHz, CD_2Cl_2) δ 295.93, 210.40, 155.81, 146.27, 139.51, 139.44 (bs), 136.75 (bs), 130.26, 130.08 (bs), 124.12, 122.51, 115.64, 82.35, 52.31, 32.78, 27.12, 21.46, 19.70 (bs); **HRMS** (FAB+) *m/z* Calcd for $C_{33}H_{42}Cl_2N_2ORu$ $[M]^+$ 654.1718, found 654.1705; **X-ray** (single-crystal) Green block crystals of X-ray diffraction quality were obtained by carefully layering pentane onto a saturated solution of **10** in DCM and allowing the biphasic mixture to stand at room temperature overnight (CCDC 1044212).[22]



11

2-adamantyloxy catalyst (11): The title compound was prepared on a 0.2 mmol scale from **21** (51 mg, 0.2 mmol) using Method C, and it was obtained as a green microcrystalline solid (106 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 16.69 (s, 1H), 7.58–7.50 (m, 1H), 7.07 (bs, 4H), 6.95–6.87 (m, 2H), 6.83–6.76 (m, 1H), 4.66–4.61 (m, 1H), 4.13 (s, 4H), 2.53 (bs, 6H), 2.44 (bs, 6H), 2.38 (bs, 6H), 2.31–2.21 (m, 3H), 1.85–1.61 (m, 8H), 1.60–1.52 (m, 1H), 1.21–1.08 (m, 2H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 299.00–298.85 (C8), 209.21, 154.00, 145.22, 140.26 (bs, C1), 139.41, 138.55 (bs, C1), 134.88 (bs), 130.51, 129.99 (bs), 123.61, 122.97, 114.35, 88.27, 52.73 (bs, C5), 51.64 (bs, C5), 38.35, 37.56, 31.57, 31.36, 27.89, 27.64, 21.40, 20.66 (bs, C6), 18.59 (bs, C6); **HRMS** (FAB+) *m/z* Calcd for $C_{38}H_{46}Cl_2N_2ORu$ $[M]^+$ 718.2031, found 718.2016; **X-ray** (single-crystal) Green block crystals of X-ray diffraction quality were obtained by carefully layering pentane onto a saturated solution of **11** in EtOAc and allowing the biphasic mixture to stand unperturbed at room temperature overnight (CCDC 1017842).[22]



12

1-adamantyloxy catalyst (12): The title compound was prepared on a 0.2 mmol scale from **22** (51 mg, 0.2 mmol) using Method C, and it was obtained as a green microcrystalline solid (114 mg, 79% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 16.48 (s, 1H), 7.46 (ddd, J_1 = 8.9 Hz, J_2 = 7.2 Hz, J_3 = 1.9 Hz, 1H), 7.24 (d, J = 8.5 Hz, 1H), 7.06 (bs, 4H), 6.93 (dd, J_1 = 7.5 Hz, J_2 = 1.7 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 4.13 (s, 4H), 2.53 (bs, 6H), 2.36 (bs, 12H), 2.23 (bs, 6H), 2.10 (bs, 3H), 1.63–1.57 (m, 6H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ 300.04 (C8), 299.94 (C8), 211.67, 152.09, 146.98, 140.69 (bs, C1), 139.23, 138.66 (bs, C1), 134.63 (bs), 129.74 (bs), 129.31, 123.78, 122.39, 117.51, 89.15, 52.60 (bs, C5), 51.47 (bs, C5), 41.09, 36.37, 32.26, 21.42, 20.75 (bs, C6), 18.61 (bs, C6); **HRMS** (FAB+) *m/z* Calcd for $C_{38}H_{46}Cl_2N_2ORu$ $[M]^+$ 718.2031, found 718.2039; **X-ray** (single-crystal) Green block crystals of X-ray diffraction quality were obtained by carefully layering pentane onto a saturated solution of **12** in EtOAc and

allowing the biphasic mixture to stand unperturbed at room temperature overnight (CCDC 1017841).[22]

X-RAY CRYSTALLOGRAPHY METHODS AND RESULTS

Refinement Details: In each case, crystals were mounted on a glass fiber or nylon loop using Paratone oil, then placed on the diffractometer under a nitrogen stream. Low temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[26] Absorption corrections were applied using SADABS.[27] Space groups were determined on the basis of systematic absences and intensity statistics, and the structures were solved by direct methods using XS[28] or by intrinsic phasing using XT (incorporated into SHELXTL) and refined by full-matrix least squares on F^2. All non-hydrogen and hydride atoms were refined using anisotropic displacement parameters. Non-hydride hydrogen atoms were placed in the idealized positions and refined using a riding model. The structure was refined (weighed least squares refinement on F^2) to convergence. Graphical representation of structures with 50% probability thermal ellipsoids was generated using Diamond visualization software.[29]

In addition to the X-ray crystal structures of catalysts **5** (Table S11 and Chart S9), **9** (Table S12 and Charts S10 and S11), **10** (Table S13 and Chart S12), **11** (Table S14 and Charts S13 and S14) and **12** (Table S15 and Charts S15 and S16), several previously published structures from the Cambridge Structural Database are discussed in this manuscript. For a detailed summary of relevant metrics, see Table S10.

Table S10: Detailed summary of relevant Ru–O and Ru=C bond lengths from X-ray structures, displayed in order of increasing k_{init}.

					Experimental (Å)				
Entry	Cat.	R^1 =	R^2 =	R^3 =	Ru–O	Ru=C	CCDC	Ref.	Solvate
1	**4**	*i*-Pr	H	H	2.2562(10)	1.8286(15)	620588	[25]	DCM
2	**9**	*c*-Pr	H	H	2.223(4) 2.249(4)	1.836(5) 1.830(5)	1044211	---	---
3	**6**	*i*-Pr	H	NO_2	2.2581(13) 2.2869(12)	1.8286(19) 1.8251(19)	698596	[30]	H_2O
4	**7**	Me	H	H	2.265(5)	1.798(9)	620589	[25]	hexane
5	**12**	1-Ada	H	H	2.2540(14) 2.2602(16)	1.828(2) 1.828(2)	1017841	---	---
6	**10**	CH_2*t*-Bu	H	H	2.2860(8)	1.8275(10)	1044212	---	DCM
7	**8**	Ph	H	H	2.305(3) 2.266(4)	1.821(5) 1.809(5)	908389	[16]	---
8	**11**	2-Ada	H	H	2.338(3) 2.355(3)	1.827(4) 1.821(4)	1017842	---	---
9	**5**	*i*-Pr	Ph	H	2.2443(4)	1.8337(5)	1017843	---	---

Table S11: Crystal data and structure analysis details for catalyst **5** (CCDC 1017843)**.**

Identification code	a14072
Empirical formula	C37 H42 Cl2 N2 O Ru
Formula weight	702.69
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 16.3602(8) Å α = 90°
	b = 13.9923(6) Å β = 101.130(2)°
	c = 15.0930(7) Å γ = 90°
Volume	3390.1(3) $Å^3$
Z	4
Density (calculated)	1.377 g/cm^3
Absorption coefficient	0.651 mm^{-1}
F(000)	1456
Crystal size	0.51 × 0.34 × 0.20 mm^3
Theta range for data collection	1.931 to 54.626°.
Index ranges	$-37 \le h \le 37$, $-31 \le k \le 31$, $-32 \le l \le 34$
Reflections collected	457990
Independent reflections	42027 [R(int) = 0.0557]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9074
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	42027 / 0 / 556
Goodness-of-fit on F^2	1.354
Final R indices [I>2σ(I)]	R1 = 0.0296, wR2 = 0.0707
R indices (all data)	R1 = 0.0518, wR2 = 0.0788
Extinction coefficient	n/a
Largest diff. peak and hole	2.335 and –0.762 $e \cdot Å^{-3}$

Chart S9: X-ray crystal structure of **5** with 50% probability ellipsoids. Hydrogen atoms omitted for clarity. CCDC 1017843.

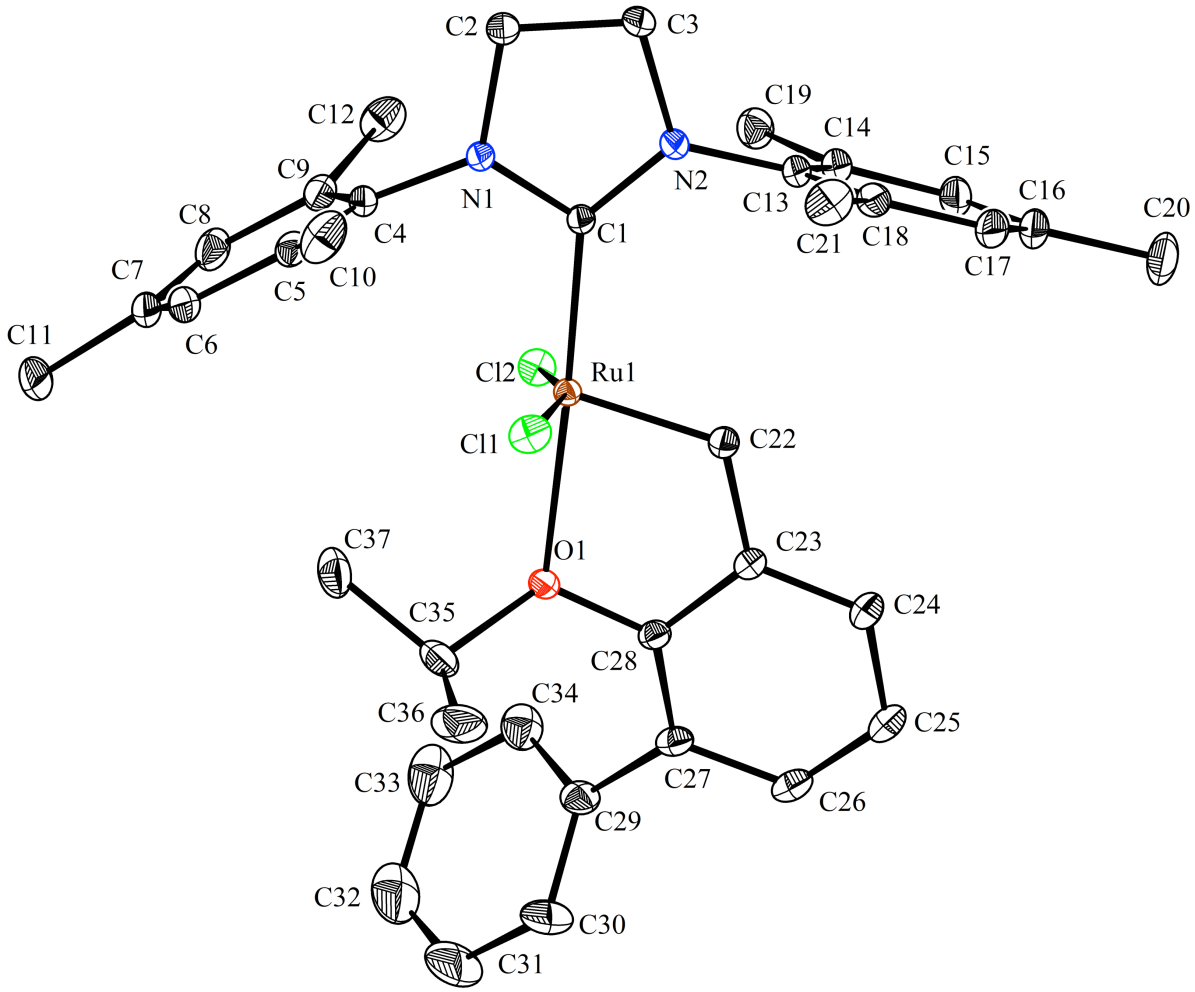


Table S12: Crystal data and structure analysis details for catalyst **9** (CCDC 1044211).

Identification code	A13226
Empirical formula	C31 H36 Cl2 N2 O Ru
Formula weight	624.59
Temperature	100(2) K
Wavelength	0.71073 Å MoK
Crystal system	orthorhombic
Space group	P n a 21
Unit cell dimensions	a = 22.9578(5) Å α = 90° b = 10.1978(2) Å β = 90° c = 24.6180(6) Å γ = 90°
Volume	5763.5(2) $Å^3$
Z	8
Density (calculated)	1.440 g/cm^3
Absorption coefficient	0.756 mm^{-1}
F(000)	2576
Crystal size	0.150 × 0.100 × 0.100 mm^3
Theta range for data collection	1.654 to 30.539°
Index ranges	$-32 \le h \le 32, -14 \le k \le 14, -35 \le l \le 35$
Reflections collected	113002
Independent reflections	17586 [R(int) = 0.0818]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6685
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17586 / 1 / 679
Goodness-of-fit on F^2	1.072
Final R indices [I>2σ(I)]	R1 = 0.0461, wR2 = 0.0991
R indices (all data)	R1 = 0.0587, wR2 = 0.1043
Absolute structure parameter	0.172(14)
Extinction coefficient	n/a
Largest diff. peak and hole	2.769 and –0.576 $e \cdot Å^{-3}$

Chart S10: X-ray crystal structure of **9** with 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Two crystallographically inequivalent molecules are present in the unit cell; for clarity, only one is shown. CCDC 1044211.

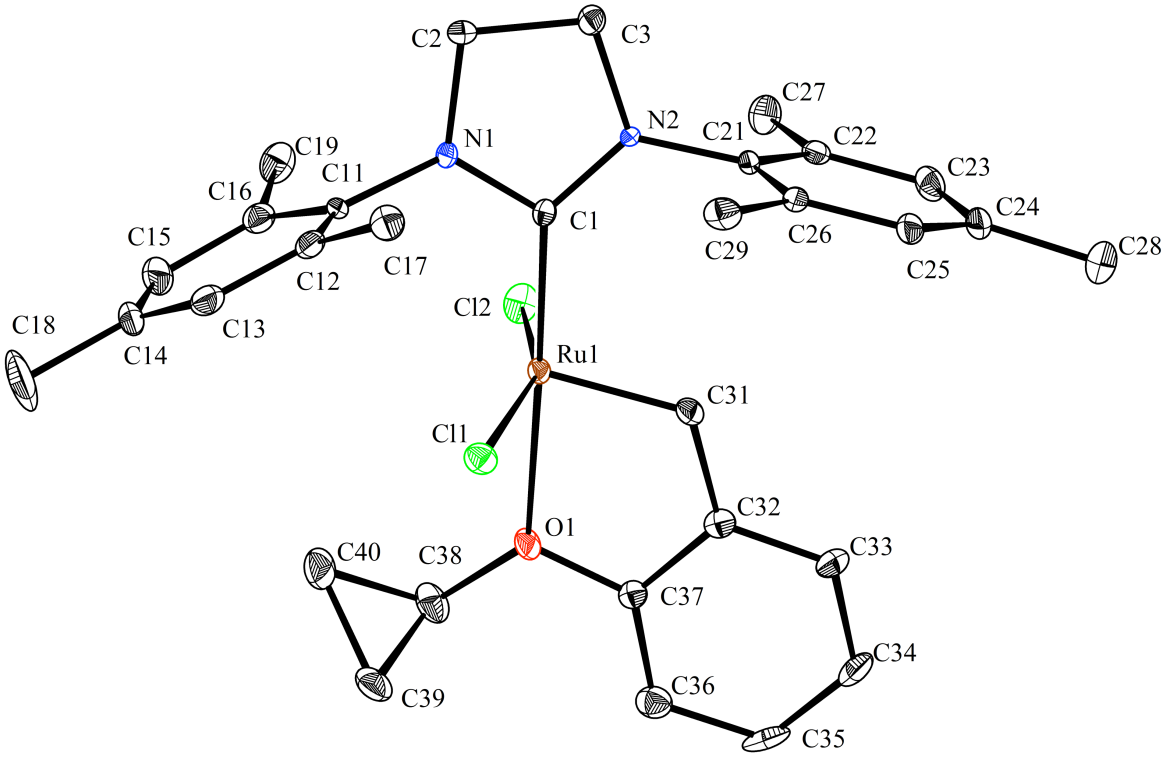


Chart S11: X-ray crystal structure of **9** with 50% probability ellipsoids (asymmetric unit). CCDC 1044211.

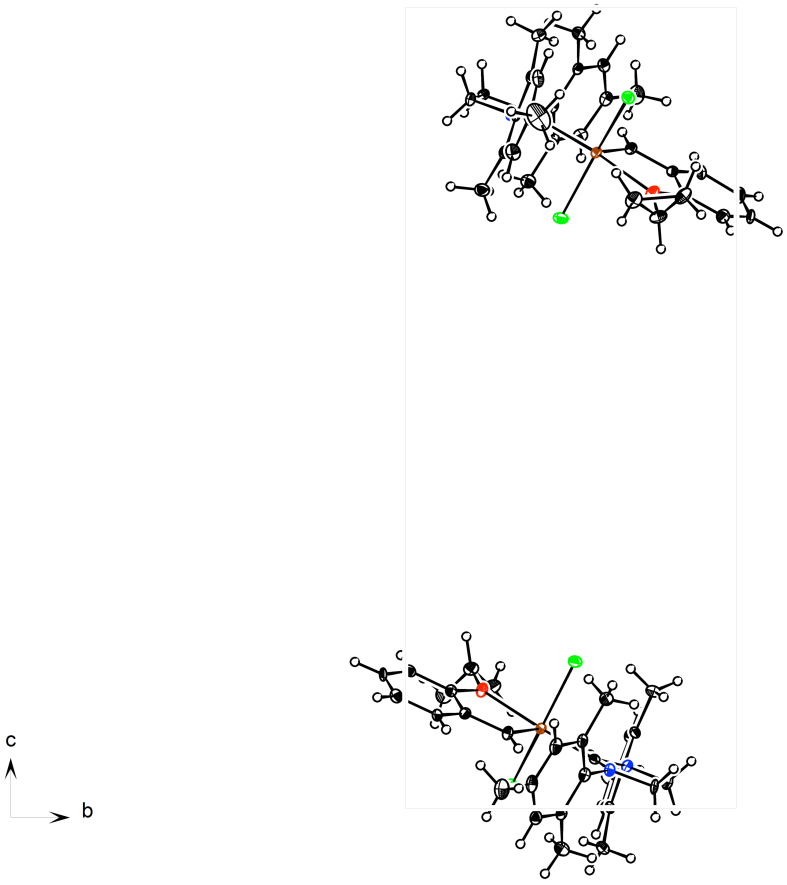


Table S13: Crystal data and structure analysis details for catalyst **10** (CCDC 1044212).

Identification code	a14086
Empirical formula	C34 H44 Cl4 N2 O Ru
Formula weight	739.58
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.6691(6) Å α = 90° b = 14.3203(7) Å β = 102.345(2)° c = 21.4702(11) Å γ = 90°
Volume	3504.8(3) $Å^3$
Z	4
Density (calculated)	1.402 g/cm^3
Absorption coefficient	0.781 mm^{-1}
F(000)	1528
Crystal size	0.600 × 0.490 × 0.450 mm^3
Theta range for data collection	1.722 to 36.469°
Index ranges	$-19 \le h \le 19, -23 \le k \le 23, -35 \le l \le 35$
Reflections collected	329568
Independent reflections	17149 [R(int) = 0.0373]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6979
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17149 / 79 / 416
Goodness-of-fit on F^2	1.170
Final R indices [I>2σ(I)]	R1 = 0.0276, wR2 = 0.0605
R indices (all data)	R1 = 0.0336, wR2 = 0.0655
Extinction coefficient	n/a
Largest diff. peak and hole	0.873 and -1.095 $e \cdot Å^{-3}$

Chart S12: X-ray crystal structure of **10** with 50% probability ellipsoids. Hydrogen atoms and DCM solvent omitted for clarity. CCDC 1044212.

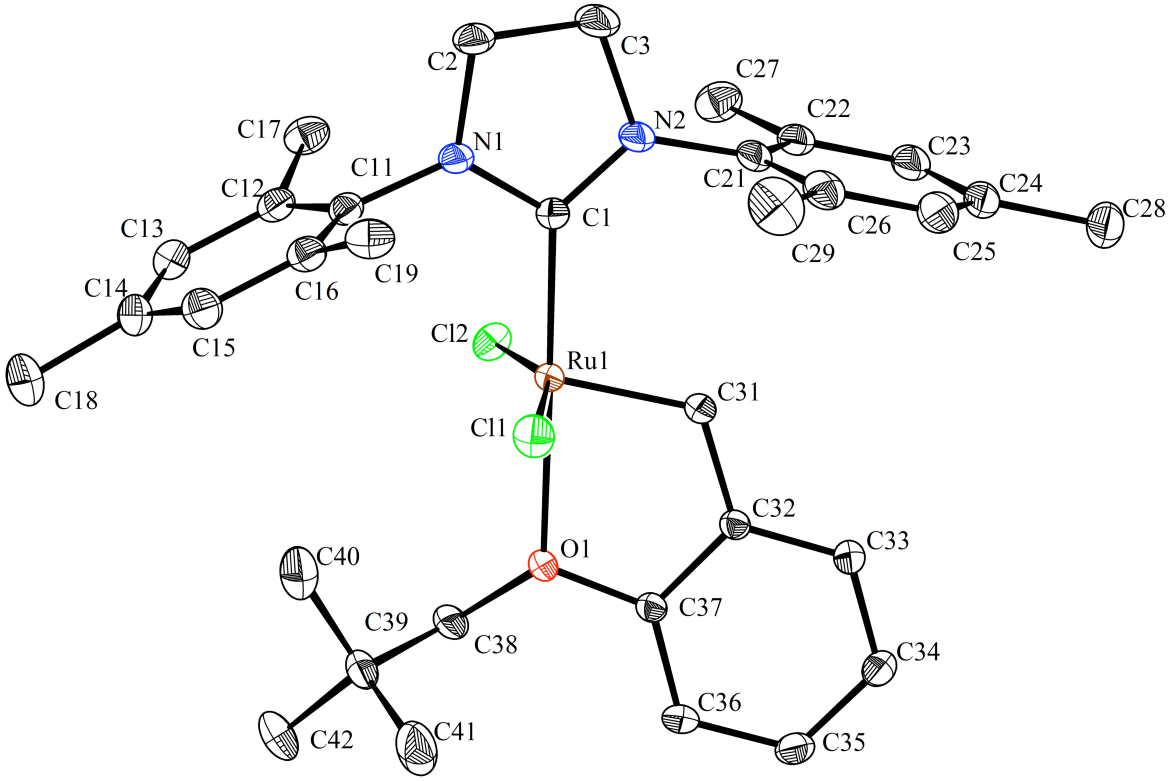


Table S14: Crystal data and structure analysis details for catalyst **11** (CCDC 1017842).

Identification code	a14021
Empirical formula	C38 H46 Cl2 N2 O Ru
Formula weight	718.74
Temperature	100 K
Wavelength	0.71073 Å MoK
Crystal system	orthorhombic
Space group	P c a 21 (# 29)
Unit cell dimensions	a = 19.0950(13) Å α = 90° b = 23.0197(14) Å β = 90° c = 15.4980(11) Å γ = 90°
Volume	6812.3(8) $Å^3$
Z	8
Density (calculated)	1.402 g/cm^3
Absorption coefficient	0.65 mm^{-1}
F(000)	2992
Crystal size	0.06 × 0.10 × 0.19 mm^3
Theta range for data collection	1.4 to 36.6°
Index ranges	$-31 \le h \le 31, -37 \le k \le 38, -25 \le l \le 22$
Reflections collected	182274
Independent reflections	30913 [R(int) = 0.1210]
Completeness to theta = 25.000°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8945
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	30913 / 1 / 805
Goodness-of-fit on F^2	1.00
Final R indices [I>2σ(I), 17009 reflections]	R1 = 0.0561, wR2 = 0.0724
R indices (all data)	R1 = 0.1360, wR2 = 0.0890
Extinction coefficient	n/a
Largest diff. peak and hole	0.91 and –0.99 $e \cdot Å^{-3}$

Chart S13: X-ray crystal structure of **11** with 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Two crystallographically inequivalent molecules are present in the unit cell; for clarity, only one is shown. CCDC 1017842.

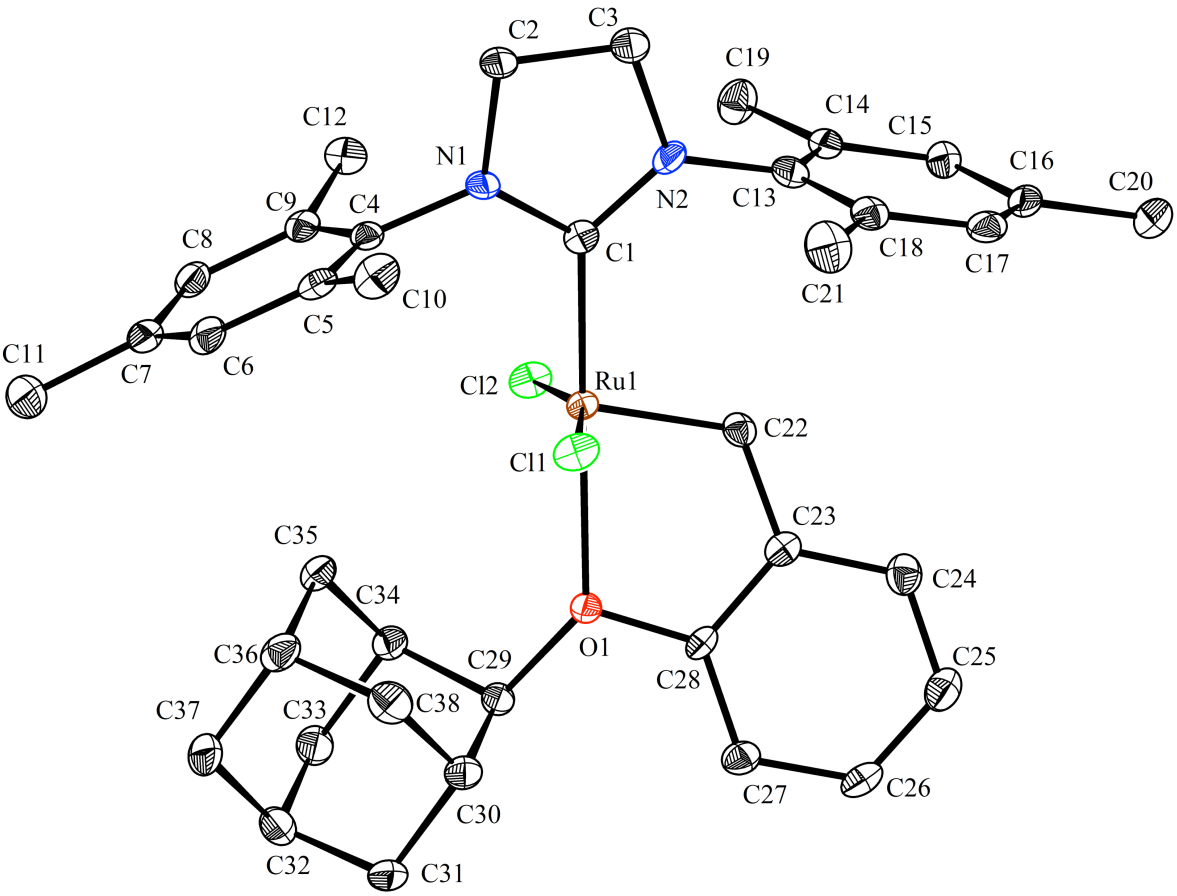


Chart S14: X-ray crystal structure of **11** with 50% probability ellipsoids (asymmetric unit). CCDC 1017842.

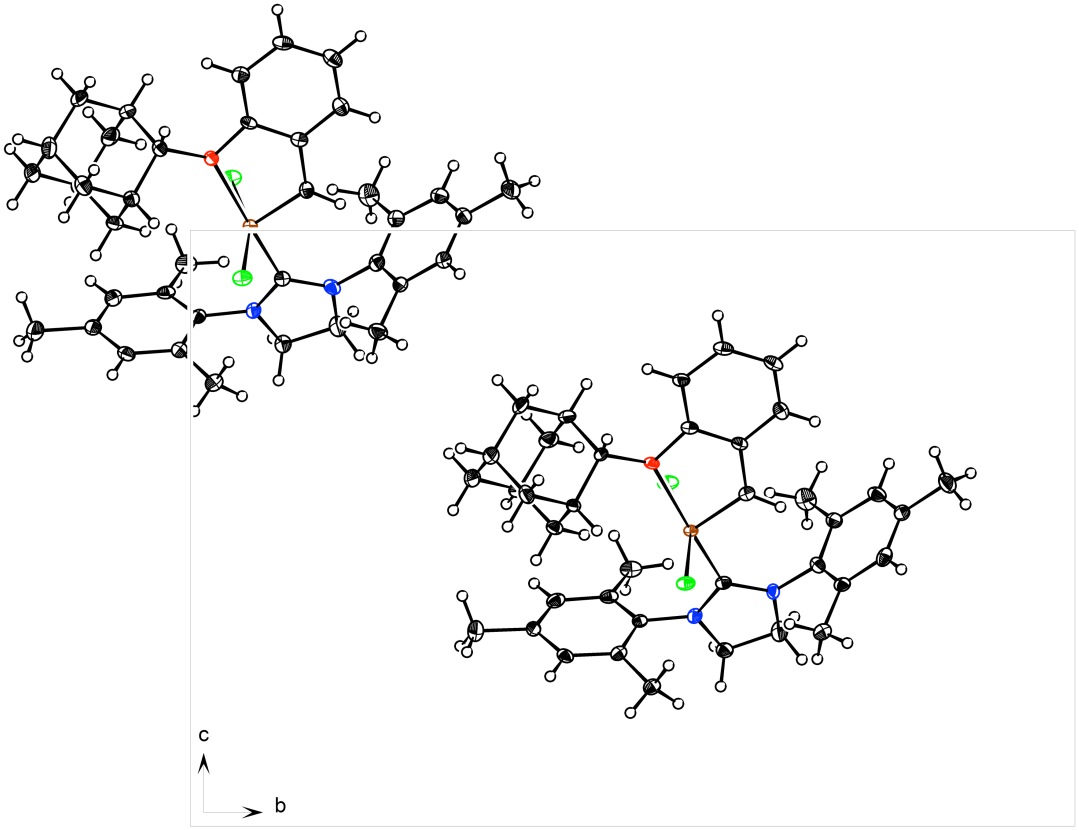


Table S15: Crystal data and structure analysis details for catalyst **12** (CCDC 1017841).

Identification code	a14014
Empirical formula	C38 H46 Cl2 N2 O Ru
Formula weight	718.74
Data collection temperature	100 K
Wavelength	0.71073 Å MoK
Crystal system	orthorhombic
Space group	P c a 21 (# 29)
Unit cell dimensions	a = 19.3436(8) Å α = 90° b = 23.1535(9) Å β = 90° c = 15.3598(6) Å γ = 90°
Volume	6879.2(5) $Å^3$
Z	8
Density (calculated)	1.388 g/cm^3
Absorption coefficient	0.64 mm^{-1}
F(000)	2992
Crystal size	0.11 × 0.42 × 0.51 mm^3
Theta range for data collection	1.9 to 41.8°
Index ranges	$-35 \le h \le 36, -42 \le k \le 43, -28 \le l \le 28$
Reflections collected	479545
Independent reflections	46262 [R(int) = 0.0578]
Completeness to theta = 25.000°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8728
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	46262 / 1 / 805
Goodness-of-fit on F^2	1.53
Final R indices [I>2σ(I), 31719 reflections]	R1 = 0.0445, wR2 = 0.0897
R indices (all data)	R1 = 0.0862, wR2 = 0.1027
Extinction coefficient	n/a
Largest diff. peak and hole	2.36 and –1.28 $e \cdot Å^{-3}$

Chart S15: X-ray crystal structure of **12** with 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Two crystallographically inequivalent molecules are present in the unit cell; for clarity, only one is shown. CCDC 1017841.

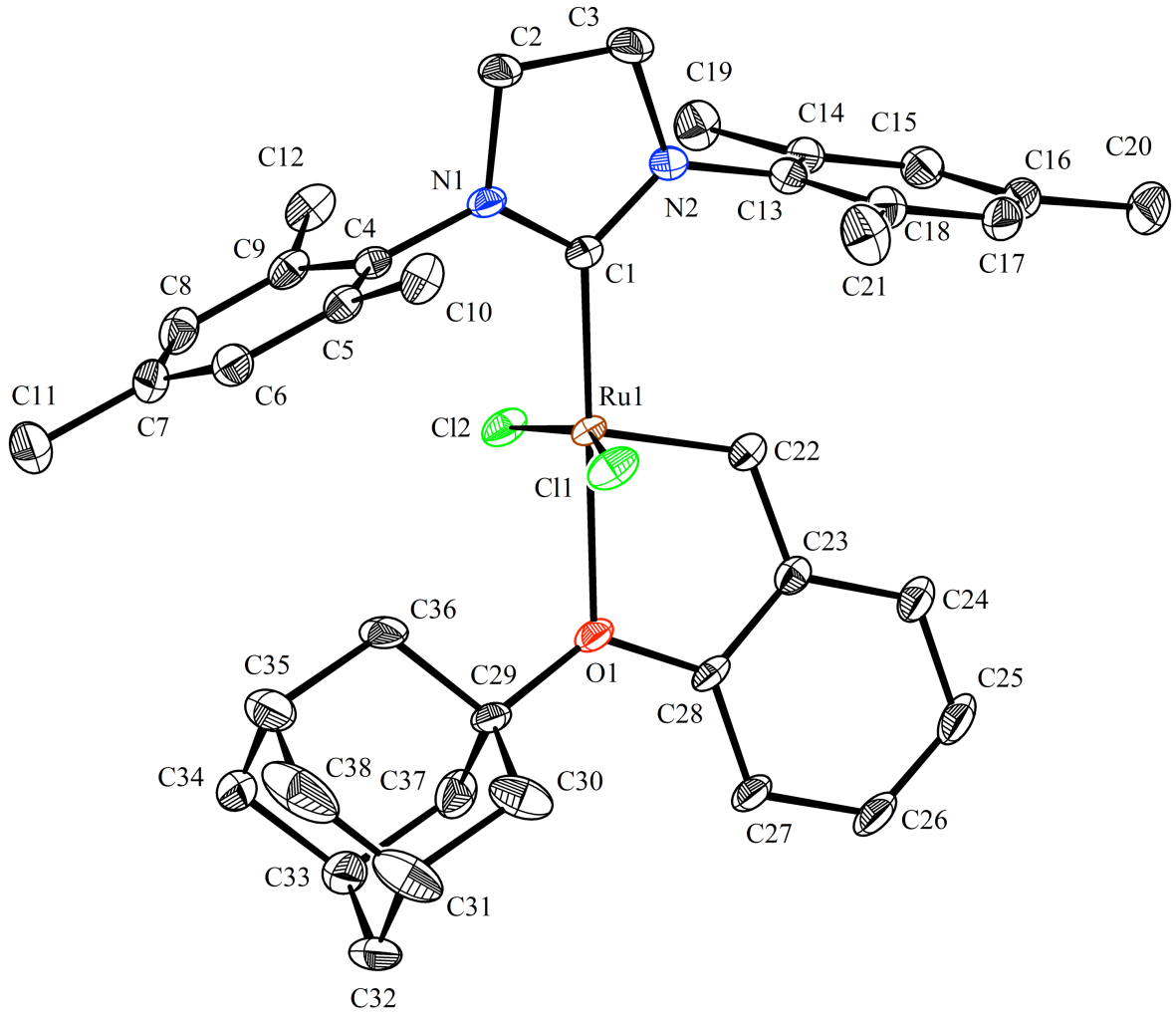
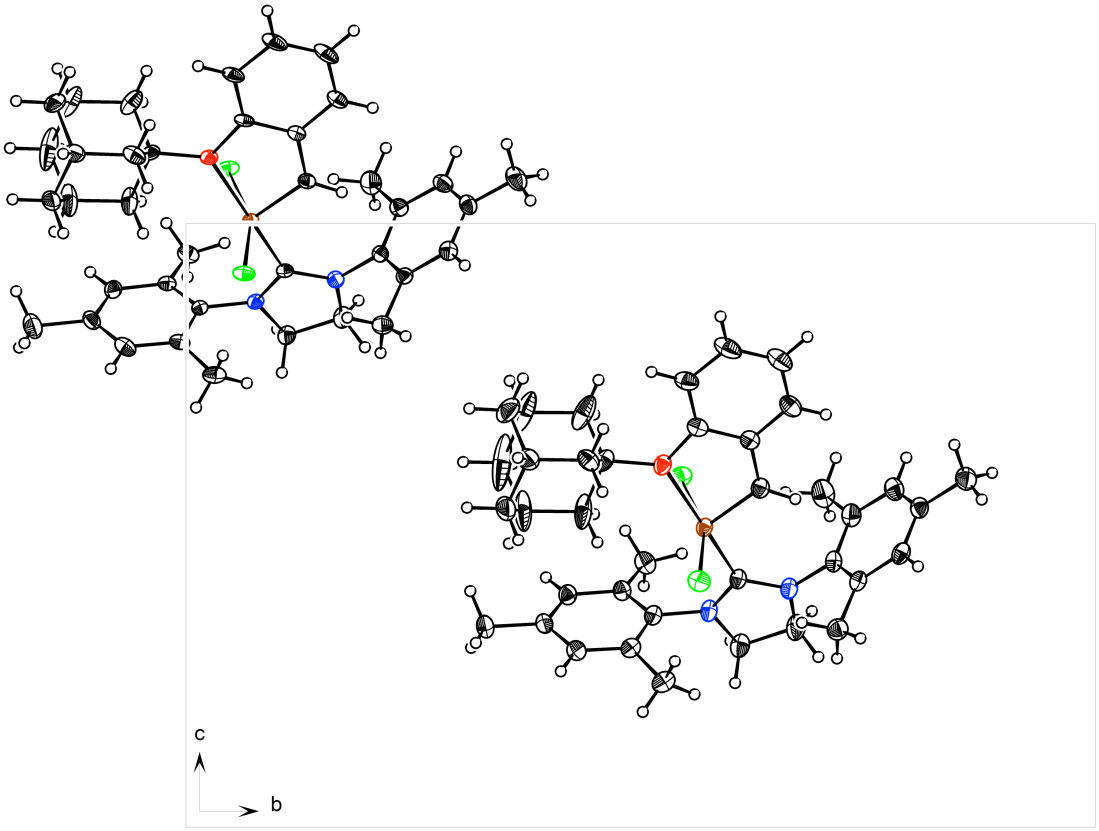


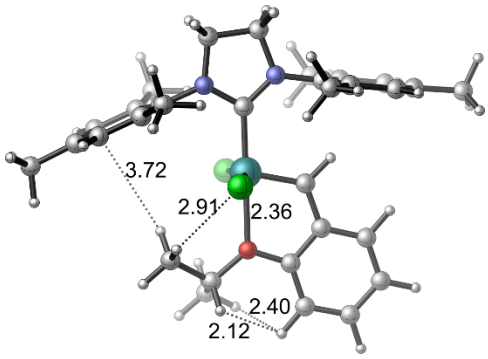
Chart S16: X-ray crystal structure of **12** with 50% probability ellipsoids (asymmetric unit). Hydrogen atoms omitted for clarity. CCDC 1017841.



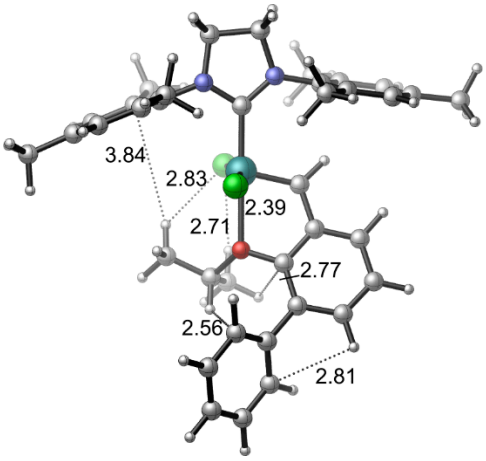
COMPUTATIONAL METHODS AND RESULTS

*3D Structures of the Optimized Geometries of Catalysts **4**–**12**:*

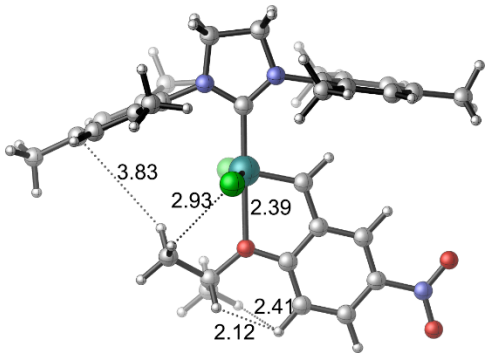
Chart S17: Optimized geometries of catalysts **4**–**12**. Geometries were optimized using B3LYP/LANL2DZ–6-31G(d) in the gas phase. All distances are shown in Å.



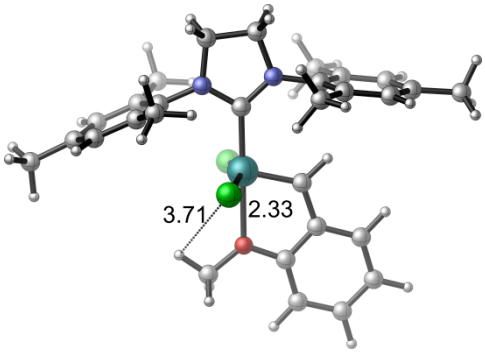
4
R^1 = *i*-Pr, R^2 = H, R^3 = H



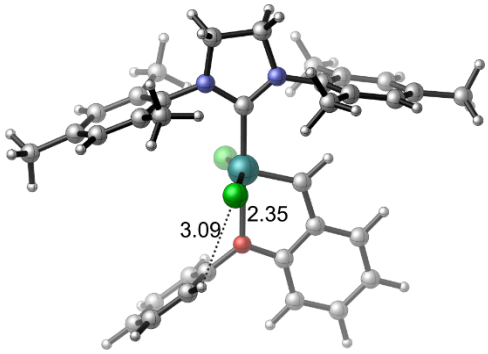
5
R^1 = *i*-Pr, R^2 = Ph, R^3 = H



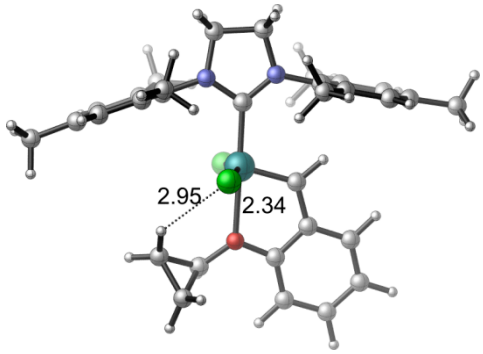
6
R^1 = *i*-Pr, R^2 = H, R^3 = NO_2



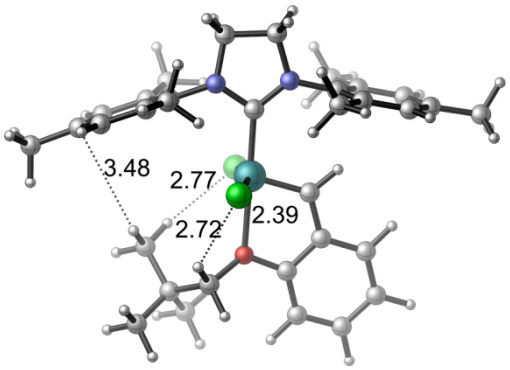
7
R^1 = Me, R^2 = H, R^3 = H



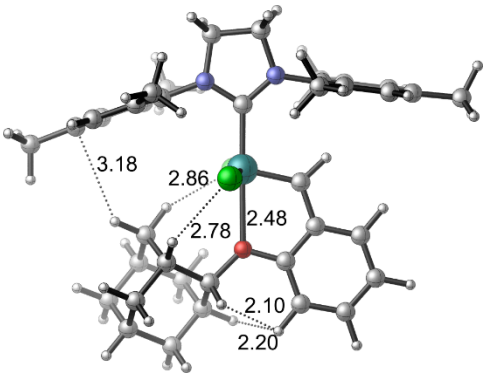
8
R^1 = Ph, R^2 = H, R^3 = H



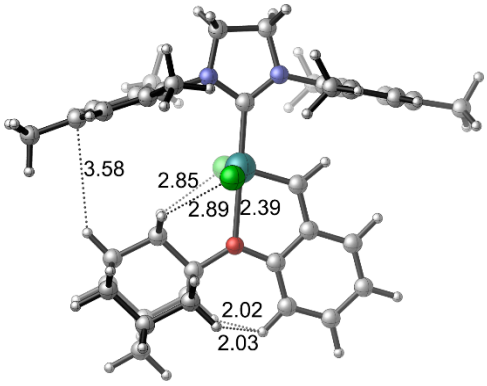
9
R^1 = Ph, R^2 = H, R^3 = H



10
R^1 = CH_2*t*-Bu, R^2 = H, R^3 = H



11
R^1 = 2-Ada, R^2 = H, R^3 = H



12
R^1 = 1-Ada, R^2 = H, R^3 = H

The B3LYP-optimized geometries of the Hoveyda-type catalysts **4**–**12** are shown above in Chart S17. The distance between the alkoxy substituent and the *N*-Mes group in **11** (3.18 Å) is much shorter than any other catalyst. This is consistent with unfavorable steric repulsion between the 2-Ada and the *N*-Mes groups. The 2-Ada group is also placed closer to the chloride ligands than in other catalysts. The shortest H···Cl distance between the 2-Ada group and the chloride ligands in **11** is 2.78 Å, shorter than those of catalysts **4**, **6**, **7**, **8**, **9** and **12** (2.91, 2.93, 3.71, 3.09, 2.95, and 2.85 Å, respectively). However, the H···Cl distances in catalysts **5** (2.71 Å) and **10** (2.72 Å) are both shorter than that of **11**, indicating some steric repulsions between the alkoxy group and the chloride in catalysts **5**, **10**, and **11**. The repulsion between the relatively small *i*-Pr group and the Cl in catalyst **5** is due to repulsion with the *ortho*-phenyl group, which pushes the *i*-Pr group (R^1) of **5** out of the plane, toward one of the chloride ligands.

In comparison, the R^1···*N*-Mes and R^1···Cl distances in 1-Ada-substituted catalyst **12** are both longer than those in **11**. Steric repulsion between two methylene groups of the 1-adamantyl group and the benzylidene is observed (the H···H distances are only 2.02 and 2.03 Å). However, this repulsion is not released after Ru–O bond dissociation and thus does not affect the Ru–O bond strength.

No unfavorable steric interactions are observed in the other fast-initiating catalyst **8** (R^1 = Ph). The Ru–O distance is similar to that of the isopropoxy-substituted catalyst **4**. The weaker Ru–O

bond in **8** is expected to be a result of electronic effects due to the less Lewis basic phenoxy oxygen atom.

Distortion Analysis Fragment Overlays and Summary Table:

Overlays of the distorted alkoxy phenyl fragment in catalysts **4**, **5**, **11**, and **12** and the corresponding fully optimized fragment are shown in Charts S18–S21, respectively. The extent of change in the geometries parallels the computed distortion energies of the alkoxy phenyl fragments. The overlay in Chart S18 clearly demonstrates minimal change in geometry for the isopropoxy phenyl fragment in **4**. In contrast, significant change in geometry is observed for the *ortho*-phenyl isopropoxy phenyl fragment in **5** (Chart S19). This is in agreement with the substantial distortion energy of the alkoxy phenyl fragment in **5**. The 2-adamantyl group in **11** (Chart S20) is more distorted than the 1-adamantyl group in **12** (Chart S21).

Chart S18: Overlay of the alkoxy phenyl fragment in catalyst **4** (shown in green) and the fully optimized fragment (shown in pink).

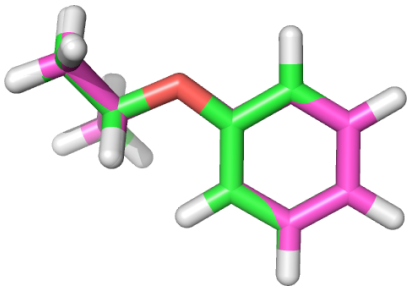


Chart S19: Overlay of the alkoxy phenyl fragment in catalyst **5** (shown in green) and the fully optimized fragment (shown in pink).

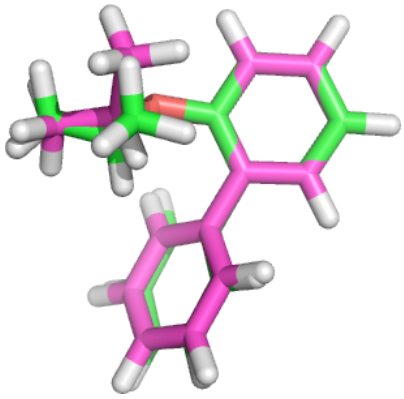


Chart S20: Overlay of the alkoxy phenyl fragment in catalyst **11** (shown in green) and the fully optimized fragment (shown in pink).

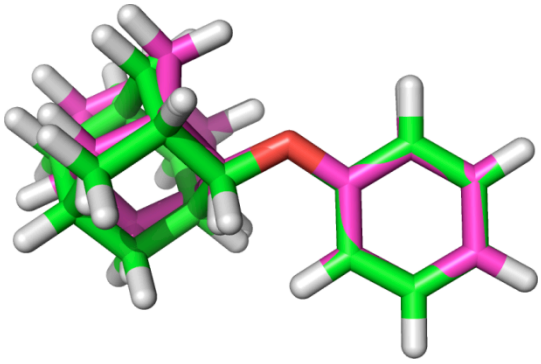


Chart S21: Overlay of the alkoxy phenyl fragment in catalyst **12** (shown in green) and the fully optimized fragment (shown in pink).

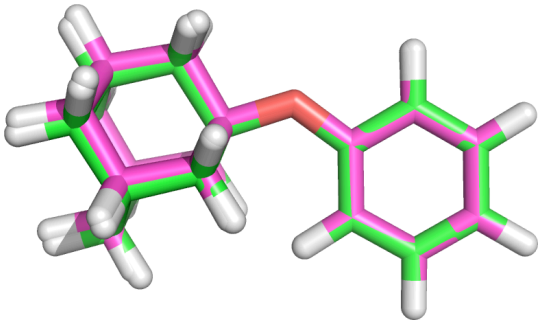
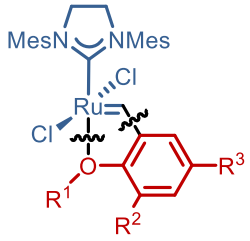


Table S16: Computed distortion energies of the SIMes–dichlororuthenium methylidene fragment (A, shown in blue) and the alkoxy phenyl fragment (B, in red) in catalysts **4**–**12**, displayed in order of increasing k_{init}



					Distortion energies (kcal/mol)		
Entry	Cat.	R^1 =	R^2 =	R^3 =	ΔE_{dist}(A)	ΔE_{dist}(B)	ΔE_{dist}(A)+ΔE_{dist}(B)
1	**4**	*i*-Pr	H	H	2.5	1.1	3.6
2	**9**	*c*-Pr	H	H	2.8	1.2	4.0
3	**6**	*i*-Pr	H	NO_2	2.1	1.0	3.1
4	**7**	Me	H	H	2.4	1.1	3.5
5	**12**	1-Ada	H	H	3.3	1.3	4.6
6	**10**	CH_2*t*-Bu	H	H	2.8	1.5	4.3
7	**8**	Ph	H	H	2.8	1.4	4.2
8	**11**	2-Ada	H	H	3.4	2.0	5.4
9	**5**	*i*-Pr	Ph	H	3.3	4.0	7.3

Comparison of Optimized Geometries Using Different Computational Methods:

Chart S22: Experimental (X-ray) Ru–O bond lengths versus computed (B3YLP) Ru–O bond lengths.

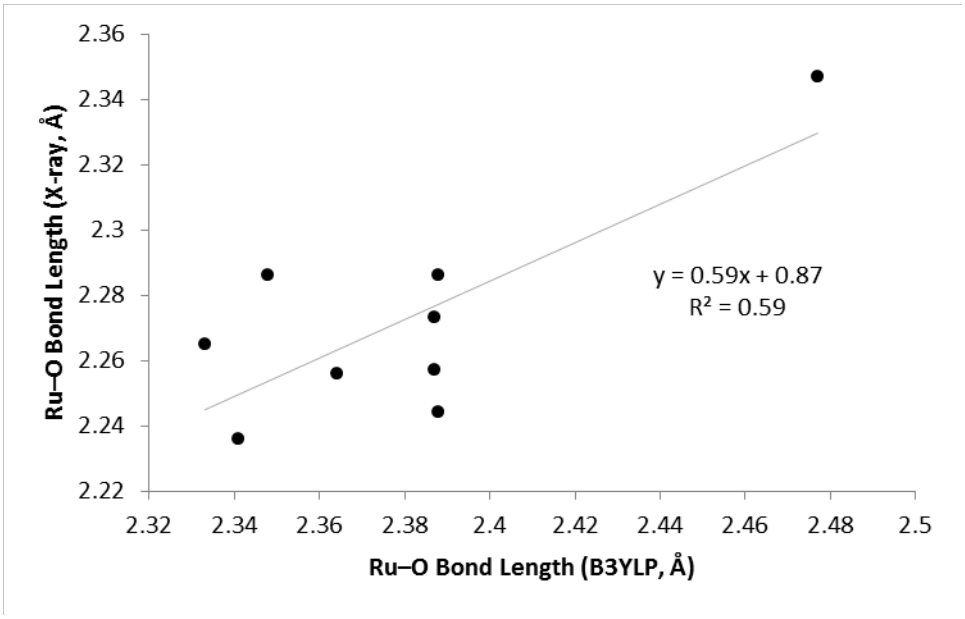


Chart S23: Experimental (X-ray) Ru–O bond lengths versus computed (BP86) Ru–O bond lengths.

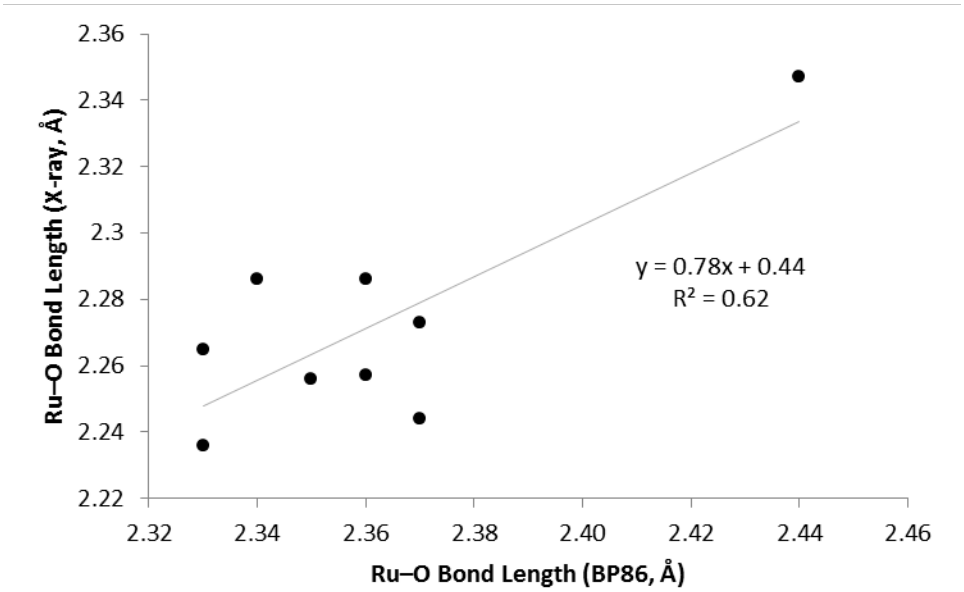


Chart S24: Experimental (X-ray) Ru–O bond lengths versus computed (M06) Ru–O bond lengths.

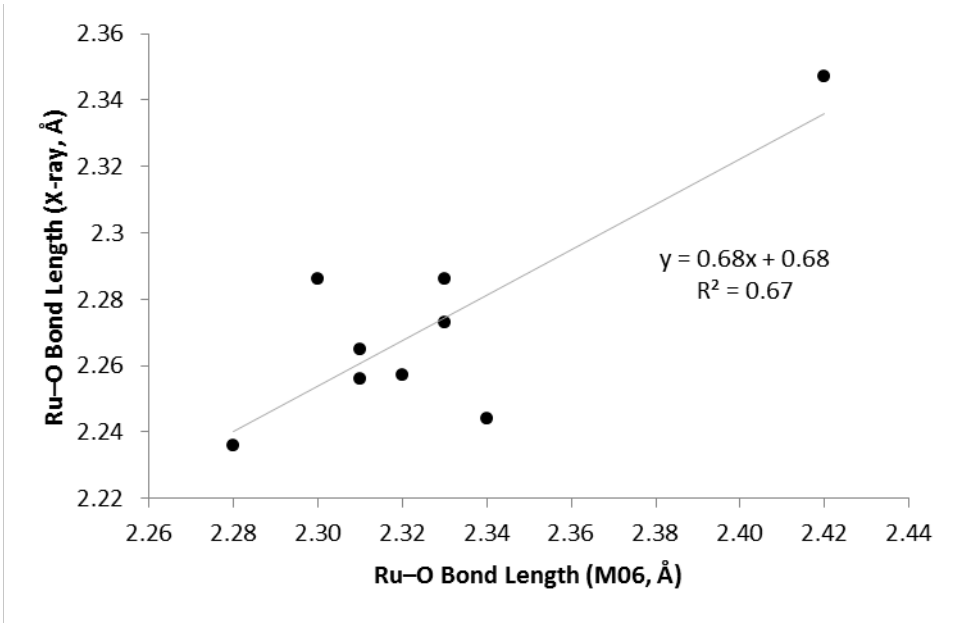


Chart S25: Experimental (X-ray) Ru–O bond lengths versus computed (M06-L) Ru–O bond lengths.

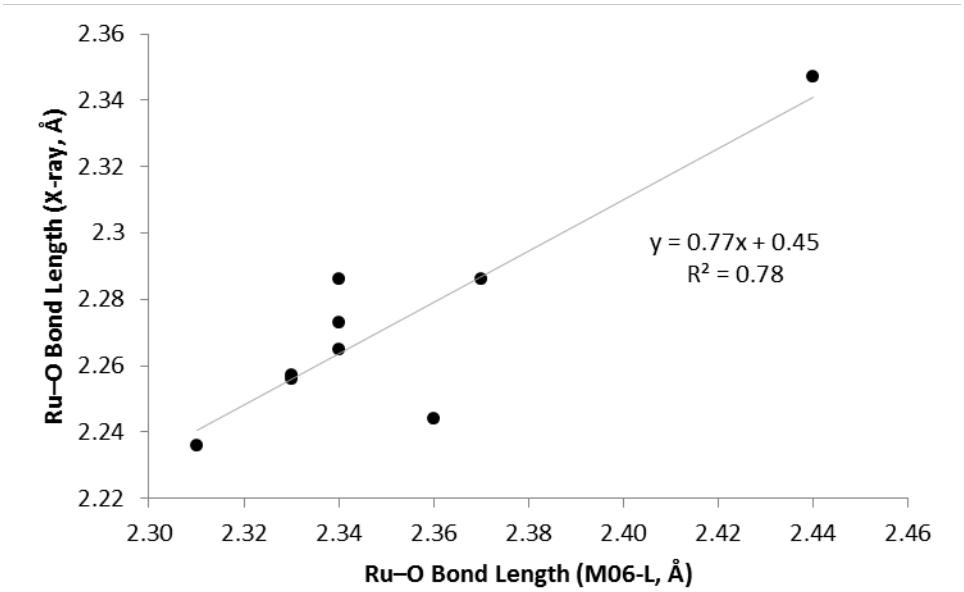
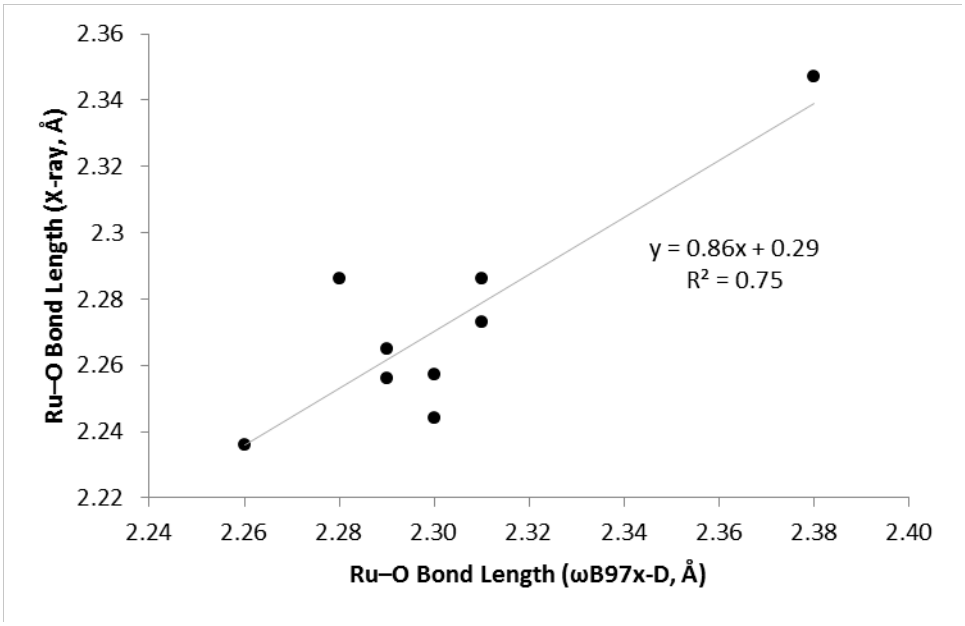


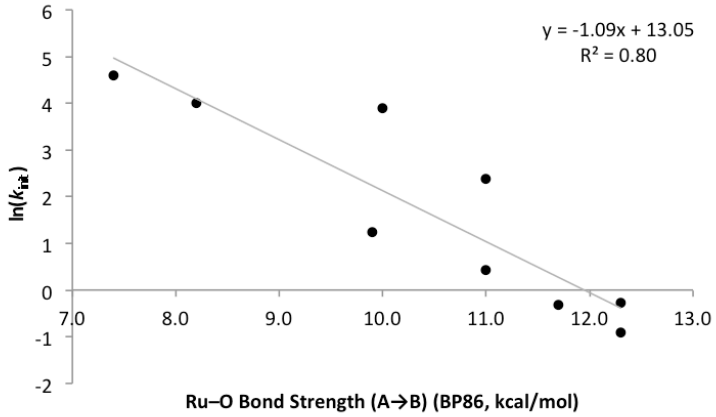
Chart S26: Experimental (X-ray) Ru–O bond lengths versus computed (ωB97x-D) Ru–O bond lengths.



Comparison of Ru–O Bond Strengths Using Different Computational Methods:

Table S17: Computed Ru–O bond strengths using BP86, displayed in increasing order of k_{init}.

					Ru–O Bond Strength (kcal/mol)	
Entry	Cat.	R^1 =	R^2 =	R^3 =	ΔG_r(**A**→**B**)	ΔG_r(**A**→**C**)
1	**4**	*i*-Pr	H	H	12.3	5.9
2	**9**	*c*-Pr	H	H	11.7	5.2
3	**6**	*i*-Pr	H	NO_2	12.3	5.4
4	**7**	Me	H	H	11.0	3.5
5	**12**	1-Ada	H	H	9.9	5.3
6	**10**	CH_2*t*-Bu	H	H	11.0	2.5
7	**8**	Ph	H	H	10.0	3.2
8	**11**	2-Ada	H	H	8.2	2.7
9	**5**	*i*-Pr	Ph	H	7.4	2.1



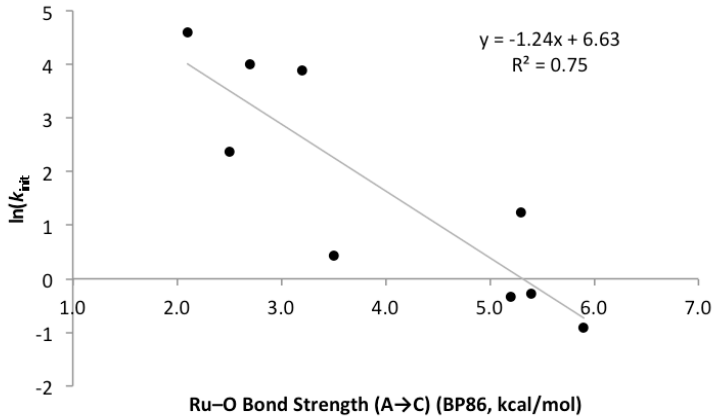
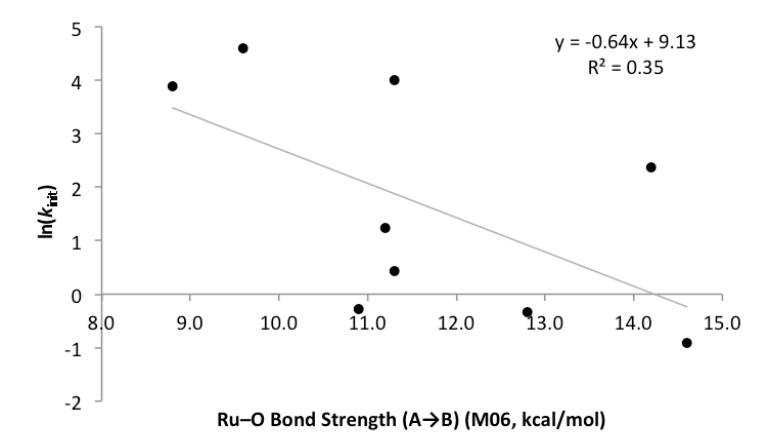


Table S18: Computed Ru–O bond strengths using M06, displayed in increasing order of k_{init}.

					Ru–O Bond Strength (kcal/mol)	
Entry	Cat.	R^1 =	R^2 =	R^3 =	ΔG_r(**A**→**B**)	ΔG_r(**A**→**C**)
1	**4**	*i*-Pr	H	H	14.6	9.4
2	**9**	*c*-Pr	H	H	12.8	9.0
3	**6**	*i*-Pr	H	NO_2	10.9	6.5
4	**7**	Me	H	H	11.3	7.9
5	**12**	1-Ada	H	H	11.2	7.9
6	**10**	CH_2*t*-Bu	H	H	14.2	7.2
7	**8**	Ph	H	H	8.8	5.5
8	**11**	2-Ada	H	H	11.3	7.4
9	**5**	*i*-Pr	Ph	H	9.6	5.2



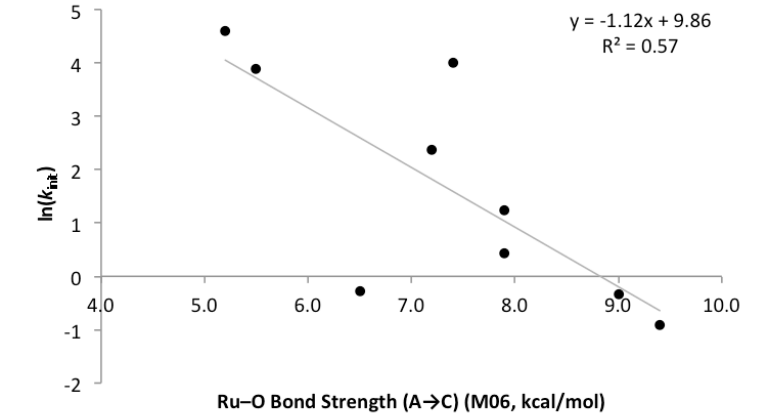
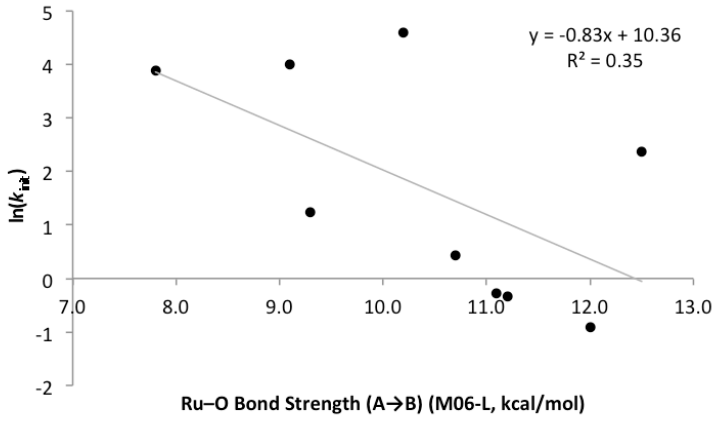


Table S19: Computed Ru–O bond strengths using M06-L, displayed in increasing order of k_{init}.

					Ru–O Bond Strength (kcal/mol)	
Entry	Cat.	R^1 =	R^2 =	R^3 =	ΔG_r(**A**→**B**)	ΔG_r(**A**→**C**)
1	**4**	*i*-Pr	H	H	12.0	6.5
2	**9**	*c*-Pr	H	H	11.2	5.5
3	**6**	*i*-Pr	H	NO_2	11.1	4.1
4	**7**	Me	H	H	10.7	4.1
5	**12**	1-Ada	H	H	9.3	3.5
6	**10**	CH_2*t*-Bu	H	H	12.5	5.3
7	**8**	Ph	H	H	7.8	2.1
8	**11**	2-Ada	H	H	9.1	4.5
9	**5**	*i*-Pr	Ph	H	10.2	3.6



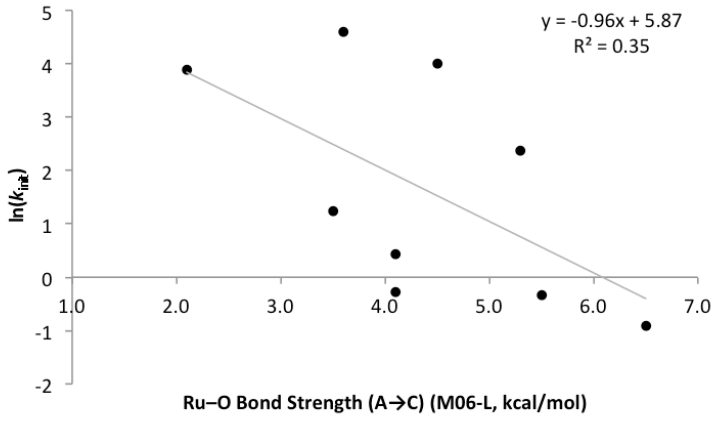
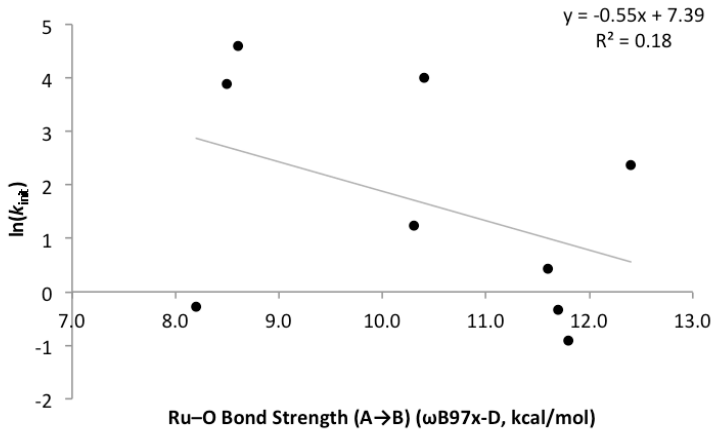
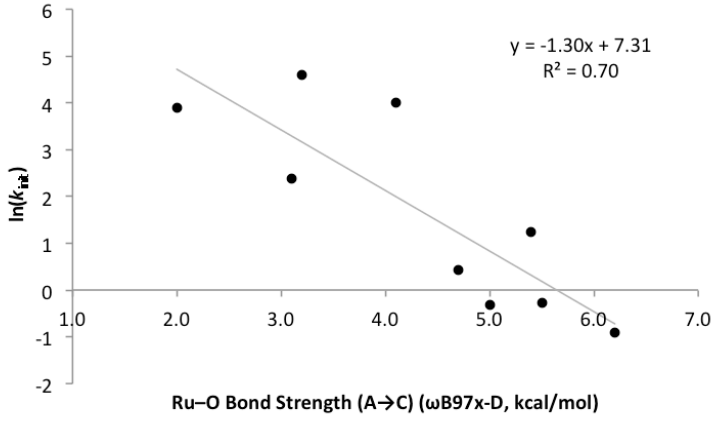


Table S20: Computed Ru–O bond strengths using ωB97x-D, displayed in increasing order of k_{init}.

					Ru–O Bond Strength (kcal/mol)	
Entry	Cat.	R^1 =	R^2 =	R^3 =	ΔG_r(**A**→**B**)	ΔG_r(**A**→**C**)
1	**4**	*i*-Pr	H	H	11.8	6.2
2	**9**	*c*-Pr	H	H	11.7	5.0
3	**6**	*i*-Pr	H	NO_2	8.2	5.5
4	**7**	Me	H	H	11.6	4.7
5	**12**	1-Ada	H	H	10.3	5.4
6	**10**	CH_2*t*-Bu	H	H	12.4	3.1
7	**8**	Ph	H	H	8.5	2.0
8	**11**	2-Ada	H	H	10.4	4.1
9	**5**	*i*-Pr	Ph	H	8.6	3.2





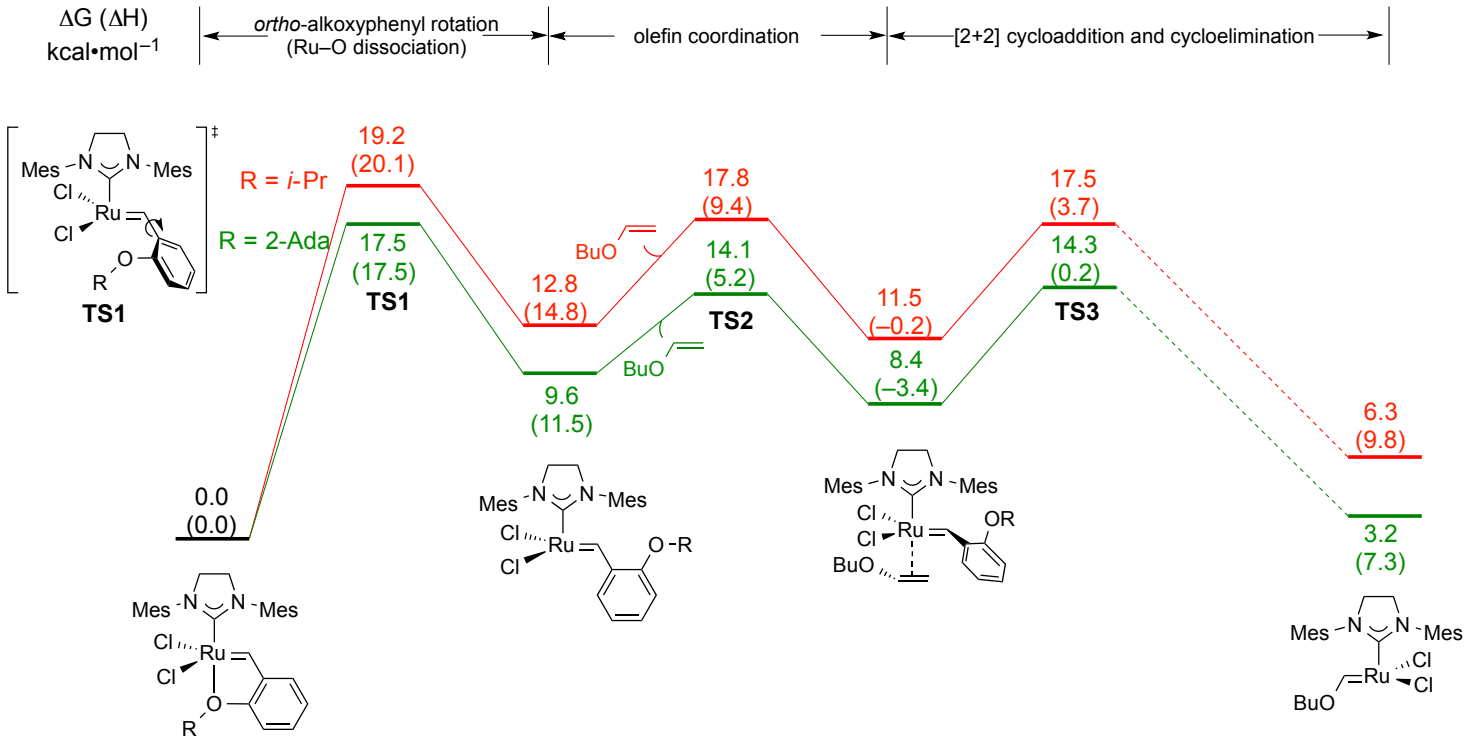
*Computed Potential Energy Profiles of the Dissociative Pathway in the Initiation of Catalysts **4** and **11**:*

The dissociative initiation pathway involves three key steps: (1) Ru–O bond dissociation via rotation of the *ortho*-alkoxyphenyl group to generate a 14-electron complex, (2) coordination of the olefin to form a 16-electron π-complex, and (3) [2+2] cycloaddition to form a metallacyclobutane intermediate and subsequent cycloelimination to form a Fischer carbene complex.

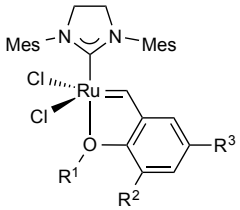
The reaction coordinates of the dissociative initiation pathway of catalysts **4** (R = *i*-Pr) and **11** (R = 2-Ada) were computed (Chart S27). The cycloelimination step was not computed since it is known to occur faster than cycloaddition (**TS3**) due to the formation of stable Fischer carbene complexes.

The calculations indicate that Ru–O bond dissociation (**TS1**) is the rate-determining step in the dissociative pathway for both catalysts. Due to the weaker Ru–O bond, all transition states and intermediates with the 2-Ada catalyst **11** are more stable than the corresponding structures with the *i*-Pr-substituted catalyst **4**.

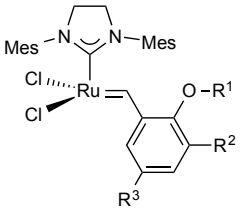
Chart S27. Potential energy profiles of the dissociative initiation pathway of catalysts **4** (R = *i*-Pr) and **11** (R = 2-Ada). Calculations were performed at the M06/SDD-6-311+G(d,p)/SMD(toluene)//B3LYP/LANL2DZ-6-31G(d) level of theory. Gibbs free energies and enthalpies (in parenthesis) are given in kcal/mol and are with respect to the corresponding reactant (the Hoveyda-type catalyst **4** or **11**) in each reaction.



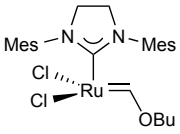
The Cartesian Coordinates (Å) and M06 Single Point Energies for the Optimized Structures:



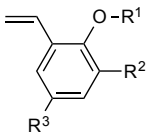
A



B



C



D

BVE

Cat.	R^1 =	R^2 =	R^3 =
4	*i*-Pr	H	H
5	*i*-Pr	Ph	H
6	*i*-Pr	H	NO_2
7	Me	H	H
8	Ph	H	H
9	*c*-Pr	H	H
10	CH_2*t*-Bu	H	H
11	2-Ada	H	H
12	1-Ada	H	H

For Cartesian coordinates listed below, the geometry optimizations were performed with B3LYP/LANL2DZ–6-31G(d). Single point energies listed below were calculated with M06/SDD–6-311+G(d,p) and the SMD solvation model in toluene.

4-A

M06 SCF energy: -2403.63067734 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.175061	0.494306	-0.037406
C	0.207469	-1.513613	0.014188
N	-0.779462	-2.445562	0.056434
C	-0.278531	-3.833844	0.097226
C	1.244645	-3.651213	0.037578
N	1.393646	-2.186512	0.010910
H	1.688461	-4.094227	-0.860990
H	1.755940	-4.069449	0.911364
H	-0.672241	-4.403196	-0.751454
H	-0.611200	-4.328445	1.016643
C	2.713904	-1.614532	-0.018596
C	3.388717	-1.369707	1.196070
C	4.666877	-0.803140	1.140410

C	5.300738	-0.518494	-0.071814
C	4.641816	-0.861798	-1.256035
C	3.363437	-1.428147	-1.258158
H	5.183079	-0.592520	2.074786
H	5.138370	-0.696950	-2.210114
C	2.773061	-1.910363	-2.561877
H	3.083239	-2.948228	-2.753649
H	1.685024	-1.862512	-2.570006
H	3.130716	-1.302649	-3.397697
C	2.827149	-1.790903	2.533216
H	3.191520	-1.137422	3.330703
H	3.153223	-2.814182	2.771519
H	1.738936	-1.756052	2.557964
C	6.662700	0.134720	-0.104153
H	7.267212	-0.238260	-0.938340
H	7.215705	-0.043627	0.824089
H	6.575717	1.222277	-0.228818
C	-2.199226	-2.248466	0.076228
C	-2.861703	-2.145089	1.313576
C	-4.253102	-1.996974	1.304406
H	-4.774795	-1.903726	2.254602
C	-4.292864	-2.068489	-1.096654
C	-2.902556	-2.218560	-1.142385
H	-4.845769	-2.032091	-2.033017
C	-4.986660	-1.959401	0.113617
C	-2.182007	-2.296156	-2.467508
H	-2.896464	-2.262806	-3.295583
H	-1.606367	-3.225280	-2.566129
H	-1.476813	-1.465450	-2.590001
H	-1.514348	-3.062424	2.750811
C	-2.099820	-2.143867	2.617907
H	-2.789001	-2.068282	3.464418
H	-1.397720	-1.303395	2.672458
C	-6.492679	-1.832508	0.134854
H	-6.836185	-1.276007	1.013364
H	-6.972799	-2.819816	0.167829
H	-6.865146	-1.321432	-0.759356
Cl	0.599465	0.725879	2.328092
Cl	0.534697	0.599098	-2.422300
C	-1.632039	0.864300	-0.043252
H	-2.416109	0.110464	0.002613
C	-2.093160	2.230719	-0.129583
C	-1.144311	3.283622	-0.162384
C	-1.557119	4.612551	-0.264779
C	-2.924405	4.896246	-0.334086
C	-3.880780	3.877041	-0.298484
C	-3.462354	2.554743	-0.196387

H	-4.186526	1.744433	-0.170398
H	-4.938405	4.117034	-0.350669
H	-3.240418	5.932880	-0.414587
H	-0.840586	5.424180	-0.289580
O	0.148501	2.857601	-0.098421
C	1.257372	3.807364	-0.006562
H	1.056633	4.593708	-0.743621
C	2.517015	3.057058	-0.415761
H	3.354749	3.762835	-0.456668
H	2.391071	2.594705	-1.398133
H	2.761562	2.278169	0.314402
C	1.336561	4.381346	1.405625
H	2.166400	5.095110	1.465433
H	1.506375	3.572732	2.122138
H	0.417348	4.902886	1.688378

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M06 SCF energy: -2403.60671542 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.594833	-0.719159	0.525147
C	-1.149319	1.094624	-0.017425
N	-0.460019	2.266530	-0.067981
C	-1.312907	3.414413	-0.438667
C	-2.724861	2.823049	-0.372843
N	-2.459475	1.378243	-0.269037
H	-3.281650	3.167607	0.506775
H	-3.323121	3.039073	-1.262915
H	-1.049479	3.771300	-1.442151
H	-1.162341	4.239453	0.263417
Cl	-0.936246	-2.000839	-1.455184
Cl	-0.997055	-0.284992	2.845941
C	-3.550809	0.448169	-0.404659
C	-3.839771	-0.059288	-1.689800
C	-4.913160	-0.940192	-1.826217
C	-5.709412	-1.312578	-0.737128
C	-5.440076	-0.734928	0.504513
C	-4.382913	0.164489	0.695315
C	-4.230698	0.854567	2.030383
H	-3.187859	1.035449	2.294294
H	-4.761018	1.818016	2.025918
H	-4.670381	0.249045	2.828597
H	-6.075467	-0.976346	1.354012
C	-6.828613	-2.312823	-0.905913

H	-6.443545	-3.340380	-0.869880
H	-7.334202	-2.191164	-1.870469
H	-7.577970	-2.215932	-0.113390
H	-5.131800	-1.348240	-2.810536
C	-3.039091	0.351115	-2.902221
H	-2.017403	-0.035140	-2.846624
H	-3.498700	-0.044524	-3.812989
H	-2.985517	1.442562	-3.004332
C	0.954905	2.499639	-0.000320
C	1.721296	2.396227	-1.176904
C	3.077399	2.732974	-1.114209
C	3.679049	3.160769	0.073645
C	2.884401	3.258848	1.219748
C	1.521641	2.942068	1.209160
C	0.696421	3.076563	2.466056
H	0.235410	2.123978	2.747860
H	1.319340	3.418188	3.298202
H	-0.116119	3.804451	2.342566
C	1.117790	1.900920	-2.471456
H	0.775996	0.862624	-2.383253
H	0.250554	2.496245	-2.781155
H	1.853655	1.945707	-3.279983
H	3.676512	2.659796	-2.019184
H	3.333327	3.597012	2.151252
C	5.153570	3.488062	0.123359
H	5.742150	2.614416	0.434022
H	5.362813	4.289173	0.840440
H	5.528419	3.802863	-0.856374
C	1.247103	-0.644823	0.423090
H	1.765718	0.106244	-0.168593
C	2.073774	-1.719578	0.949758
C	1.714758	-2.448106	2.104907
C	2.512390	-3.477502	2.593584
C	3.691464	-3.805239	1.923782
C	4.080321	-3.111635	0.775650
C	3.287033	-2.070711	0.281071
H	4.997035	-3.395716	0.273214
H	4.323514	-4.609252	2.292011
H	2.220541	-4.013077	3.491682
H	0.816388	-2.155089	2.638956
O	3.582957	-1.341632	-0.826597
C	4.689196	-1.696818	-1.681246
H	5.563008	-1.921615	-1.055551
C	4.985653	-0.450087	-2.506633
H	4.120579	-0.189406	-3.125836
H	5.212212	0.398252	-1.853976
H	5.843251	-0.627224	-3.164463

C	4.329150	-2.903118	-2.548649
H	3.465128	-2.666163	-3.178409
H	4.076516	-3.777155	-1.941598
H	5.171978	-3.167657	-3.197367

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M06 SCF energy: -502.56223068 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.250019	1.935455	-0.025443
H	-0.309896	2.378820	-0.341253
C	-1.289892	0.464080	-0.061384
C	-0.077936	-0.272079	-0.120758
C	-0.102751	-1.672010	-0.156114
C	-1.321748	-2.352751	-0.140923
C	-2.523061	-1.647201	-0.093615
C	-2.494246	-0.254596	-0.059238
H	-3.428946	0.298720	-0.050364
H	-3.472931	-2.173872	-0.092935
H	-1.323015	-3.439158	-0.170506
H	0.818748	-2.240814	-0.189936
O	1.064777	0.477347	-0.145409
C	2.363193	-0.139376	-0.188598
H	2.330166	-0.991669	-0.880262
C	-2.240274	2.747916	0.367889
H	-3.193746	2.380163	0.738608
H	-2.119274	3.826846	0.340820
C	3.302466	0.919360	-0.757596
H	4.320707	0.523207	-0.835455
H	2.972423	1.232416	-1.752910
H	3.322143	1.800671	-0.107226
C	2.782487	-0.605456	1.206733
H	2.069696	-1.323525	1.622760
H	3.768460	-1.082729	1.170025
H	2.837933	0.252086	1.886191

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M06 SCF energy: -2634.55534627 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.238365	0.192156	0.229340

Cl	0.661748	0.562553	2.597899
Cl	-0.454911	0.493060	-2.062216
O	-2.133733	0.051815	0.518846
N	2.820192	1.515215	-0.332957
N	3.166840	-0.646574	-0.287350
C	2.208556	0.307819	-0.163290
C	4.283152	1.412609	-0.473700
H	4.775445	1.815142	0.420058
H	4.628201	1.984401	-1.340080
C	4.494498	-0.097341	-0.629302
H	4.767151	-0.382270	-1.652872
H	5.257368	-0.494985	0.046567
C	2.205199	2.817203	-0.290533
C	2.156276	3.538147	0.919394
C	1.539517	4.796130	0.914588
H	1.478070	5.346612	1.851293
C	1.026295	5.367505	-0.250514
C	1.189499	4.670487	-1.453177
H	0.851090	5.124058	-2.382184
C	1.788341	3.409876	-1.504340
C	2.832309	3.063997	2.184059
H	3.815313	3.547314	2.282042
H	2.966813	1.983789	2.209350
H	2.244552	3.333909	3.065855
C	0.325472	6.705457	-0.220213
H	0.509244	7.275996	-1.137327
H	0.653474	7.312059	0.630566
H	-0.761554	6.578131	-0.130679
C	2.037482	2.751214	-2.839552
H	1.650544	3.376996	-3.649436
H	1.549973	1.776370	-2.905078
H	3.112159	2.610983	-3.018353
C	3.022322	-2.073373	-0.258228
C	2.695779	-2.762971	-1.440926
C	2.608577	-4.158424	-1.384771
H	2.347179	-4.701457	-2.290643
C	2.846008	-4.870535	-0.204082
C	3.172917	-4.150235	0.950014
H	3.353285	-4.685869	1.879642
C	3.272023	-2.754505	0.947845
C	2.406782	-2.031479	-2.730211
H	2.181769	-2.742298	-3.531090
H	3.262011	-1.427168	-3.058102
H	1.551915	-1.353227	-2.626185
C	2.781585	-6.380633	-0.184095
H	2.500753	-6.757781	0.804989
H	3.755702	-6.821528	-0.435363

H	2.057292	-6.761221	-0.912255
C	3.590553	-2.005797	2.220343
H	4.497888	-1.396478	2.120123
H	3.753000	-2.704533	3.046595
H	2.775688	-1.326565	2.498477
C	-0.035951	-1.623896	0.364070
H	0.756532	-2.361583	0.485294
C	-1.379770	-2.154212	0.295126
C	-1.611593	-3.535922	0.156624
H	-0.762248	-4.213455	0.182441
C	-2.902444	-4.012056	-0.034252
H	-3.089218	-5.076509	-0.141107
C	-3.956161	-3.103876	-0.147520
H	-4.953809	-3.466330	-0.379507
C	-3.774094	-1.713028	-0.028644
C	-2.477231	-1.258438	0.274522
C	-4.923513	-0.818388	-0.341585
C	-6.179483	-1.019338	0.251842
H	-6.296853	-1.797242	1.002061
C	-7.268749	-0.219890	-0.098504
H	-8.232467	-0.384195	0.376465
C	-7.119170	0.789070	-1.051426
H	-7.966796	1.411760	-1.324883
C	-5.873788	0.994057	-1.651948
H	-5.751210	1.773348	-2.399469
C	-4.783055	0.198384	-1.303558
H	-3.815206	0.358780	-1.771774
C	-2.953627	0.875688	1.435965
H	-3.963962	0.877268	1.027930
C	-2.959334	0.282481	2.839470
H	-3.378401	-0.729435	2.840330
H	-3.589696	0.904796	3.485875
H	-1.948084	0.251131	3.252683
C	-2.387361	2.284953	1.355739
H	-1.387932	2.338016	1.796661
H	-3.045525	2.964838	1.909085
H	-2.340027	2.618688	0.314459

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M06 SCF energy: -2634.53923637 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	1.215374	-0.691553	-0.492894
C	2.152812	0.985708	-0.040307

N	1.731891	2.279105	-0.032469
C	2.823101	3.231412	0.258462
C	4.072505	2.346951	0.190599
N	3.500338	0.989971	0.168506
H	4.659870	2.522444	-0.718447
H	4.732817	2.469023	1.054252
H	2.677906	3.681893	1.248049
H	2.828741	4.036097	-0.482098
Cl	1.357698	-1.989769	1.497882
Cl	1.614443	-0.434221	-2.836316
C	4.371922	-0.146497	0.323673
C	4.584074	-0.652863	1.623807
C	5.452360	-1.734506	1.778381
C	6.120227	-2.310083	0.691899
C	5.942356	-1.738198	-0.568998
C	5.093959	-0.643514	-0.778903
C	5.051480	0.008078	-2.140999
H	4.055505	0.365936	-2.405865
H	5.748294	0.857805	-2.182538
H	5.362446	-0.700213	-2.914847
H	6.488153	-2.141534	-1.419262
C	7.009216	-3.516352	0.882444
H	6.419436	-4.442400	0.872212
H	7.536026	-3.479334	1.842462
H	7.756347	-3.595528	0.085804
H	5.609327	-2.139561	2.775609
C	3.919768	-0.040114	2.833301
H	2.845303	-0.245242	2.834691
H	4.342332	-0.458857	3.751703
H	4.057858	1.047747	2.869086
C	0.395594	2.802602	-0.071267
C	-0.326346	2.918674	1.133345
C	-1.591082	3.510680	1.091212
C	-2.146615	3.983809	-0.103195
C	-1.393240	3.869200	-1.273723
C	-0.118120	3.290418	-1.285208
C	0.668702	3.203864	-2.570678
H	0.928944	2.168925	-2.815229
H	0.091231	3.619585	-3.401871
H	1.608956	3.767596	-2.509306
C	0.229679	2.396000	2.438363
H	0.452207	1.324194	2.382211
H	1.160973	2.901167	2.723266
H	-0.486983	2.550538	3.250438
H	-2.157421	3.603630	2.015539
H	-1.804199	4.241504	-2.209495
C	-3.533613	4.582017	-0.122872

H	-4.299068	3.795812	-0.087125
H	-3.705524	5.168136	-1.031280
H	-3.701878	5.235585	0.740690
C	-0.568576	-0.222697	-0.356521
H	-0.897109	0.650589	0.202334
C	-1.634871	-1.080139	-0.854413
C	-1.404844	-2.032945	-1.874212
C	-2.430916	-2.843381	-2.337963
C	-3.717778	-2.693930	-1.820904
C	-4.008602	-1.749022	-0.824157
C	-2.950418	-0.962582	-0.320334
H	-4.532589	-3.291759	-2.220000
H	-2.241387	-3.565373	-3.126640
H	-0.420116	-2.093469	-2.326653
O	-3.169732	-0.037746	0.667649
C	-3.494172	-0.540789	2.000246
H	-4.217677	-1.355839	1.885045
C	-4.152194	0.619096	2.734666
H	-3.466455	1.471753	2.788959
H	-5.064722	0.935664	2.221378
H	-4.412548	0.319684	3.755709
C	-2.243845	-1.060705	2.701941
H	-1.523202	-0.253685	2.870827
H	-1.741385	-1.840349	2.122294
H	-2.515825	-1.485936	3.675465
C	-5.421266	-1.587366	-0.376691
C	-6.031711	-0.321753	-0.336264
C	-6.196427	-2.712716	-0.050530
C	-7.373927	-0.190039	0.018693
H	-5.448491	0.556527	-0.592420
C	-7.538579	-2.579591	0.308283
H	-5.736967	-3.697612	-0.065879
C	-8.132750	-1.317303	0.343786
H	-7.831093	0.796078	0.034152
H	-8.117767	-3.463336	0.562807
H	-9.178036	-1.211814	0.621457

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M06 SCF energy: -733.49297841 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.320832	0.355177	-0.608564
H	-2.981495	1.273073	-1.079876
C	-2.252049	-0.608446	-0.292167

C	-0.906078	-0.177321	-0.267050
C	0.149614	-1.082728	-0.018640
C	-0.175166	-2.419533	0.255807
C	-1.498997	-2.858233	0.251833
C	-2.522260	-1.964478	-0.039812
H	-3.548002	-2.317469	-0.090783
H	-1.725413	-3.903487	0.443033
H	0.630425	-3.126742	0.432333
O	-0.645075	1.148357	-0.541591
C	-0.192816	1.984639	0.557812
H	0.619283	1.458817	1.074676
C	-4.628778	0.200289	-0.363753
H	-5.036985	-0.673427	0.138118
H	-5.343980	0.963684	-0.655633
C	0.353804	3.251327	-0.087033
H	0.714118	3.944051	0.681244
H	1.183691	3.013272	-0.758726
H	-0.430020	3.753497	-0.665356
C	-1.324439	2.261810	1.546069
H	-1.735276	1.332080	1.951824
H	-0.947398	2.859786	2.384092
H	-2.138272	2.815555	1.065453
C	1.583890	-0.682459	-0.075664
C	2.097079	0.044646	-1.164315
C	2.472454	-1.081348	0.936971
C	3.453933	0.358928	-1.234202
H	1.425971	0.355938	-1.957552
C	3.829680	-0.763720	0.867781
H	2.090278	-1.633600	1.791529
C	4.326068	-0.042328	-0.218917
H	3.832843	0.913380	-2.089009
H	4.497498	-1.077917	1.665757
H	5.382700	0.205326	-0.275310

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M06 SCF energy: -2608.10308260 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.437010	-0.391376	0.050979
C	-1.143297	1.489802	0.038754
N	-0.523662	2.696401	0.034212
C	-1.460941	3.837630	0.065999
C	-2.834025	3.153710	0.126826
N	-2.485006	1.723338	0.083000

H	-3.475423	3.412643	-0.722467
H	-3.380420	3.381815	1.048476
H	-1.331799	4.454690	-0.829931
H	-1.259414	4.466203	0.939580
C	-3.538688	0.742411	0.053764
C	-4.091155	0.277546	1.267322
C	-5.102896	-0.685858	1.205724
C	-5.604153	-1.161038	-0.010193
C	-5.101262	-0.608077	-1.190379
C	-4.087842	0.356475	-1.186927
H	-5.519450	-1.062065	2.137771
H	-5.513011	-0.925356	-2.146255
C	-3.696728	1.011578	-2.490834
H	-4.422165	1.798199	-2.745114
H	-2.702066	1.454525	-2.455803
H	-3.698626	0.284885	-3.307439
C	-3.703366	0.857657	2.606689
H	-3.909967	0.145373	3.410689
H	-4.295195	1.761739	2.812169
H	-2.645702	1.113445	2.661497
C	-6.664688	-2.236564	-0.045589
H	-7.277259	-2.166655	-0.950699
H	-7.329946	-2.173949	0.822435
H	-6.211934	-3.237025	-0.035538
C	0.878561	2.987185	-0.046987
C	1.611130	3.176023	1.140100
C	2.969220	3.492424	1.030467
H	3.549354	3.627779	1.940792
C	2.837287	3.444035	-1.367920
C	1.475544	3.126017	-1.313696
H	3.313078	3.541191	-2.341308
C	3.600897	3.633143	-0.210846
C	0.694022	2.887038	-2.584604
H	1.318891	3.081329	-3.461404
H	-0.185164	3.539737	-2.655153
H	0.332909	1.853268	-2.646616
H	0.118509	3.670578	2.639943
C	0.972382	2.996418	2.496950
H	1.694449	3.206724	3.291557
H	0.600850	1.973887	2.633104
C	5.063068	4.005276	-0.296393
H	5.642377	3.542665	0.509697
H	5.198688	5.091866	-0.212101
H	5.501105	3.693815	-1.249940
Cl	-0.619083	-0.583539	2.442411
Cl	-0.928194	-0.809622	-2.264648
C	1.379511	-0.120467	-0.065037

H	1.853724	0.852234	-0.176111
C	2.290615	-1.244648	0.005767
C	1.770919	-2.564646	0.098351
C	2.628548	-3.668019	0.188486
C	4.005676	-3.466947	0.189031
C	4.517680	-2.171085	0.093785
C	3.680376	-1.064815	0.001592
H	4.104470	-0.069987	-0.068016
H	4.690977	-4.302527	0.260550
H	2.242010	-4.676563	0.258071
O	0.419577	-2.619321	0.101051
C	-0.299123	-3.900502	0.053989
H	0.192579	-4.557061	0.780440
C	-0.230247	-4.477563	-1.356476
H	-0.775928	-5.427405	-1.387816
H	0.799133	-4.666877	-1.675623
H	-0.687366	-3.778145	-2.062203
C	-1.720642	-3.621101	0.518030
H	-2.260976	-4.571322	0.596635
H	-2.247115	-2.985910	-0.202014
H	-1.721503	-3.129603	1.494365
N	5.968271	-1.974925	0.092031
O	6.390054	-0.820118	0.013260
O	6.682116	-2.976281	0.169380

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M06 SCF energy: -2608.07881691 a.u.

Cartesian coordinates

ATOM	X	Y	Z
N	-2.835315	-1.270076	-0.236364
C	-3.322300	-2.576779	-0.711562
C	-2.028517	-3.389014	-0.824079
N	-0.981475	-2.352650	-0.703965
C	-1.481325	-1.147839	-0.320964
H	-3.827940	-2.458978	-1.677285
H	-4.035983	-3.000889	0.000451
H	-1.933491	-3.912485	-1.779386
H	-1.922043	-4.127304	-0.019741
Ru	-0.617955	0.616313	-0.100614
Cl	-0.848333	1.167341	-2.406326
Cl	-0.978272	1.111699	2.195835
C	-3.783488	-0.278734	0.205207
C	-4.446132	0.537024	-0.732116
C	-5.369350	1.473789	-0.249656

C	-5.675432	1.585148	1.107605
C	-5.061053	0.697916	1.998740
H	-5.316766	0.741331	3.055021
H	-5.870552	2.123086	-0.964237
H	-4.521594	1.306368	-2.742832
H	-3.244226	0.119685	-2.500609
C	-4.266986	0.377698	-2.223565
H	-4.939391	-0.402830	-2.608314
C	-6.642974	2.633263	1.604365
H	-7.342014	2.939606	0.819197
H	-7.225393	2.269683	2.458121
H	-6.108054	3.532819	1.936221
C	-4.123638	-0.244627	1.574576
C	-3.525389	-1.215726	2.564006
H	-3.686403	-2.257938	2.258945
H	-2.449220	-1.056015	2.672134
H	-3.983593	-1.085633	3.548954
C	0.382708	-2.781683	-0.831340
C	1.057370	-3.262622	0.306795
C	2.352242	-3.766645	0.143660
C	2.978104	-3.807412	-1.106414
C	2.275327	-3.323296	-2.214116
C	0.975911	-2.815627	-2.107028
H	2.747161	-3.343635	-3.194112
H	2.882563	-4.137628	1.017906
C	0.427708	-3.206782	1.680082
H	-0.510161	-3.773347	1.728811
H	1.104145	-3.628641	2.429355
C	0.246740	-2.320874	-3.332822
H	0.878437	-2.420792	-4.220447
H	-0.671539	-2.893678	-3.516823
H	-0.043887	-1.269859	-3.233200
C	4.364895	-4.387448	-1.263374
H	4.932202	-4.331624	-0.328309
H	4.933652	-3.861990	-2.037957
H	4.320921	-5.445327	-1.555029
H	0.194721	-2.177090	1.975637
C	1.168973	0.192262	0.019863
H	1.522488	-0.807993	0.261295
C	2.187920	1.239414	0.003339
C	3.346702	1.107762	0.833964
C	4.330654	2.108512	0.836296
C	4.191824	3.231979	0.029911
C	3.063442	3.359392	-0.777625
C	2.068123	2.387409	-0.797614
H	1.220486	2.501269	-1.464345
H	4.944551	4.010600	0.019313

H	5.205329	2.023985	1.468376
O	3.400915	-0.012580	1.583497
C	4.451678	-0.223649	2.557491
H	5.408543	0.070611	2.108544
C	4.470454	-1.724494	2.818892
H	3.515883	-2.049207	3.246424
H	5.269640	-1.972184	3.525419
H	4.640079	-2.275219	1.889008
C	4.172171	0.592577	3.818490
H	4.126857	1.665095	3.608378
H	3.213874	0.291071	4.253862
H	4.961378	0.422313	4.559242
N	2.931244	4.545057	-1.628341
O	1.921290	4.644870	-2.322608
O	3.844329	5.373916	-1.595637

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M06 SCF energy: -707.03706973 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.522224	2.418914	0.214884
H	1.573484	2.438011	0.486256
C	-0.063388	1.075155	0.069718
C	0.788430	-0.054898	-0.089636
C	0.244412	-1.343403	-0.224159
C	-1.132325	-1.532190	-0.209277
C	-1.962857	-0.425469	-0.048821
C	-1.442025	0.858139	0.096270
H	-2.127429	1.682718	0.246201
H	-1.566388	-2.518905	-0.311711
H	0.887836	-2.205947	-0.343569
O	2.115166	0.217336	-0.120744
C	3.106712	-0.831291	-0.212844
H	2.765560	-1.570836	-0.947902
C	-0.118647	3.579769	0.028340
H	-1.158149	3.636980	-0.284096
H	0.391938	4.526447	0.176454
C	4.365762	-0.153774	-0.741171
H	5.167244	-0.889826	-0.863891
H	4.173245	0.317120	-1.709798
H	4.707833	0.617617	-0.042835
C	3.314273	-1.488127	1.151145
H	2.389101	-1.928656	1.534532
H	4.065903	-2.281888	1.077994

H	3.665403	-0.745456	1.875625
N	-3.412099	-0.617856	-0.014504
O	-4.122229	0.378758	0.133107
O	-3.841226	-1.767262	-0.137167

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M06 SCF energy: -2325.03310022 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.202983	0.707457	0.000155
C	-0.429962	-1.285545	0.000088
N	0.462756	-2.309203	0.000212
C	-0.169895	-3.643262	0.000210
C	-1.669222	-3.312962	0.000180
N	-1.675554	-1.840894	0.000002
H	-2.186817	-3.694654	0.887068
H	-2.186844	-3.694864	-0.886603
H	0.140607	-4.209016	0.885444
H	0.140636	-4.209014	-0.885019
C	-2.934297	-1.142924	-0.000067
C	-3.571968	-0.864484	-1.227693
C	-4.789672	-0.177021	-1.198978
C	-5.401989	0.199156	-0.000259
C	-4.789877	-0.177043	1.198539
C	-3.572167	-0.864522	1.227445
H	-5.274580	0.060622	-2.143567
H	-5.274931	0.060584	2.143053
C	-3.038777	-1.367306	2.547966
H	-3.436105	-2.371643	2.756903
H	-1.950393	-1.409800	2.568726
H	-3.353824	-0.714340	3.366608
C	-3.038370	-1.367254	-2.548140
H	-3.352616	-0.713844	-3.366732
H	-3.436313	-2.371262	-2.757491
H	-1.950010	-1.410495	-2.568470
C	-6.691181	0.987236	-0.000393
H	-7.295012	0.770125	0.887306
H	-7.296102	0.768049	-0.886850
H	-6.492776	2.067401	-0.001807
C	1.895136	-2.253840	0.000026
C	2.580869	-2.259528	-1.228721
C	3.979670	-2.264884	-1.201597
H	4.521197	-2.260010	-2.145272
C	3.979992	-2.265141	1.201094

C	2.581206	-2.259767	1.228589
H	4.521764	-2.260438	2.144631
C	4.697001	-2.273500	-0.000353
C	1.838610	-2.216078	2.543244
H	2.541455	-2.223492	3.381811
H	1.171220	-3.078735	2.665368
H	1.218978	-1.315179	2.623967
H	1.169398	-3.077357	-2.664718
C	1.837943	-2.215529	-2.543175
H	2.540529	-2.224179	-3.381948
H	1.219372	-1.313906	-2.624097
C	6.207797	-2.320715	-0.000536
H	6.624775	-1.833119	-0.888136
H	6.570581	-3.357430	0.000933
H	6.625082	-1.830557	0.885520
Cl	-0.616345	0.953123	-2.357152
Cl	-0.616146	0.952826	2.357528
C	1.633316	0.908992	0.000084
H	2.342731	0.083119	0.000074
C	2.218094	2.232156	0.000030
C	1.361028	3.358913	0.000125
C	1.862765	4.657182	0.000061
C	3.250260	4.839396	-0.000108
C	4.123597	3.747611	-0.000206
C	3.607858	2.454392	-0.000132
H	4.271450	1.593400	-0.000213
H	5.197404	3.908705	-0.000336
H	3.647700	5.850680	-0.000160
H	1.200927	5.515508	0.000144
O	0.040102	3.028067	0.000298
C	-0.965531	4.040981	0.000312
H	-0.882712	4.658056	0.900924
H	-1.914934	3.507788	0.000403
H	-0.882835	4.657961	-0.900374

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M06 SCF energy: -2325.01437415 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.111787	-2.417286	-1.066974
C	-1.374736	-2.274224	0.121496
C	-1.994086	-2.324724	1.385682
C	-3.377483	-2.517655	1.429755
C	-4.144768	-2.667329	0.268349

C	-3.494560	-2.613180	-0.967116
N	0.053734	-2.172897	0.034282
C	0.848665	-1.069671	0.026298
N	2.142959	-1.498595	-0.026647
C	2.261388	-2.958589	-0.173961
C	0.824537	-3.432688	0.068123
Ru	0.435157	0.858471	0.081412
C	-1.413432	0.890719	0.035465
C	-2.165407	2.122356	0.183334
C	-1.630073	3.268186	0.813138
C	-2.357154	4.447833	0.923636
C	-3.650408	4.507224	0.401389
C	-4.221867	3.396416	-0.223255
C	-3.493434	2.208518	-0.335651
O	-3.971221	1.089072	-0.939714
C	-5.284061	1.104385	-1.477319
C	3.329026	-0.684612	-0.103580
C	3.849946	-0.323065	-1.361758
C	5.011635	0.456619	-1.394438
C	5.678408	0.844292	-0.230589
C	5.182989	0.391155	0.997008
C	4.024996	-0.384992	1.087969
C	3.260500	-0.819137	-2.661009
C	6.903861	1.725424	-0.293146
C	3.584628	-0.930383	2.425074
C	-1.203631	-2.152379	2.660894
C	-5.638518	-2.880271	0.358356
C	-1.444058	-2.324631	-2.419160
Cl	0.792930	1.187016	2.425511
Cl	0.798740	1.383532	-2.215030
H	-1.997954	0.014203	-0.229281
H	-5.227209	3.467375	-0.621217
H	-4.229444	5.423508	0.481483
H	-1.924203	5.309979	1.421272
H	-0.642281	3.201381	1.259107
H	-6.035007	1.303776	-0.701770
H	2.621868	-3.206489	-1.179798
H	2.972581	-3.361755	0.552923
H	0.463780	-4.119658	-0.703176
H	0.700918	-3.920712	1.042444
H	3.376188	-0.070197	-3.448807
H	3.783680	-1.729305	-2.989106
H	2.195764	-1.037484	-2.581256
H	5.406879	0.759326	-2.361865
H	7.445186	1.594951	-1.236276
H	7.594466	1.511722	0.529855
H	6.628198	2.785739	-0.219555

H	5.717195	0.639156	1.911503
H	3.591183	-2.028794	2.428180
H	4.265029	-0.596690	3.214224
H	2.576804	-0.598126	2.685773
H	-0.964247	-1.348950	-2.561692
H	-0.665111	-3.086865	-2.546910
H	-2.175953	-2.463284	-3.220479
H	-4.073762	-2.726338	-1.881101
H	-6.136565	-2.020135	0.823317
H	-5.880814	-3.758114	0.969836
H	-6.082945	-3.029928	-0.630868
H	-3.868146	-2.553900	2.400318
H	-0.710320	-1.174506	2.699275
H	-1.859626	-2.237390	3.532416
H	-0.419643	-2.913271	2.763664
H	-5.444664	0.107076	-1.889513
H	-5.380872	1.849658	-2.277018

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M06 SCF energy: -423.96965003 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.550652	-1.357323	-0.121428
H	0.980344	-2.239113	-0.400048
C	0.776682	-0.106528	-0.062391
C	-0.639264	-0.157186	-0.007300
C	-1.394876	1.019121	0.044713
C	-0.754887	2.260511	0.042610
C	0.635758	2.334236	-0.018250
C	1.381916	1.158309	-0.075148
H	2.463909	1.216562	-0.150575
H	1.136389	3.298004	-0.032685
H	-1.352515	3.167290	0.082209
H	-2.476976	0.977756	0.090471
O	-1.191082	-1.408538	-0.000900
C	-2.602606	-1.530275	0.020720
H	-3.032079	-1.094957	0.932807
H	-2.810401	-2.601870	0.002012
H	-3.063793	-1.056150	-0.855929
C	2.856152	-1.497822	0.145421
H	3.485000	-0.672391	0.469512
H	3.341612	-2.465090	0.055747

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M06 SCF energy: -2516.67155670 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.097249	0.197145	0.003584
C	0.629662	-1.676094	-0.001197
N	1.898251	-2.161232	0.028634
C	1.961181	-3.635433	-0.022769
C	0.492630	-4.039125	0.144858
N	-0.209387	-2.752395	-0.003061
H	0.286213	-4.468044	1.132932
H	0.155385	-4.751517	-0.613774
H	2.604817	-4.017147	0.775534
H	2.381713	-3.960906	-0.982001
C	-1.649957	-2.736652	-0.005850
C	-2.327878	-2.846191	-1.240762
C	-3.724422	-2.832274	-1.230861
C	-4.458124	-2.749151	-0.042236
C	-3.756696	-2.740822	1.164297
C	-2.357257	-2.759178	1.212841
H	-4.252789	-2.898374	-2.179458
H	-4.308225	-2.733103	2.102259
C	-1.674529	-2.908449	2.551898
H	-1.636093	-3.970527	2.835532
H	-0.662222	-2.506671	2.554507
H	-2.230554	-2.381071	3.331920
C	-1.587303	-3.044352	-2.541245
H	-2.294550	-3.117037	-3.373008
H	-1.001485	-3.973466	-2.526519
H	-0.906939	-2.215486	-2.748795
C	-5.966957	-2.678924	-0.066877
H	-6.402417	-3.059821	0.863044
H	-6.382873	-3.256076	-0.900163
H	-6.309095	-1.642508	-0.187612
C	3.136996	-1.440524	0.000072
C	3.722321	-1.117581	-1.238452
C	4.959380	-0.463466	-1.229520
H	5.417323	-0.199406	-2.180454
C	5.003606	-0.474945	1.172739
C	3.767998	-1.129386	1.218773
H	5.495932	-0.220412	2.108980
C	5.617618	-0.137896	-0.038571
C	3.116296	-1.451223	2.542760
H	3.761285	-1.147396	3.372826
H	2.921835	-2.525923	2.650843

H	2.153049	-0.938243	2.650397
H	2.830914	-2.491038	-2.668362
C	3.024142	-1.418169	-2.543999
H	3.638152	-1.095182	-3.390123
H	2.056284	-0.907132	-2.609541
C	6.971008	0.534899	-0.060020
H	7.097880	1.153242	-0.954962
H	7.781302	-0.206596	-0.059980
H	7.116363	1.172640	0.818474
Cl	-0.572893	0.257192	-2.358965
Cl	-0.501392	0.213028	2.381077
C	1.435232	1.227799	-0.010856
H	2.447676	0.828020	-0.025756
C	1.342188	2.671716	-0.000060
C	0.068402	3.282494	0.020714
C	-0.086798	4.663795	0.038220
C	1.061215	5.462073	0.031534
C	2.339449	4.893091	0.008379
C	2.475684	3.508649	-0.006480
H	3.460176	3.048232	-0.022651
H	3.219047	5.529763	0.003064
H	0.950060	6.542865	0.045415
H	-1.074969	5.108363	0.057059
O	-0.965731	2.378747	0.029879
C	-2.303109	2.799517	0.016134
C	-2.907600	3.098673	-1.202386
C	-2.995601	2.844437	1.223000
C	-4.252385	3.474187	-1.202726
H	-2.334959	3.011003	-2.119348
C	-4.341017	3.218628	1.203856
H	-2.485630	2.564117	2.138460
C	-4.967272	3.538273	-0.003565
H	-4.742311	3.707608	-2.143862
H	-4.899146	3.255232	2.135210
H	-6.014190	3.828896	-0.011573

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M06 SCF energy: -2516.65673439 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.459753	-2.475613	0.912269
C	0.629829	-2.358316	-0.219321
C	1.137708	-2.494059	-1.523672
C	2.505186	-2.754463	-1.670814

C	3.359944	-2.882744	-0.572291
C	2.818089	-2.734969	0.709886
N	-0.783737	-2.207001	-0.022435
C	-1.544117	-1.081863	-0.003594
N	-2.843961	-1.465736	0.152305
C	-2.997309	-2.916132	0.353965
C	-1.588500	-3.443297	0.058976
Ru	-1.078463	0.831057	-0.142997
C	0.767351	0.819339	-0.211626
C	1.515923	2.052565	-0.389536
C	0.944695	3.208854	-0.973195
C	1.663334	4.389907	-1.103673
C	2.982082	4.450633	-0.642684
C	3.583674	3.332944	-0.065979
C	2.863073	2.143251	0.052438
O	3.384084	1.031878	0.673588
C	-4.000016	-0.612539	0.258209
C	-4.449714	-0.195983	1.526760
C	-5.582482	0.623858	1.587479
C	-6.289503	0.999573	0.443871
C	-5.867368	0.492584	-0.790251
C	-4.741799	-0.325921	-0.909110
C	-3.818005	-0.672555	2.813388
C	-7.480726	1.924067	0.534024
C	-4.386300	-0.930479	-2.246019
C	0.251960	-2.349104	-2.738603
C	4.834305	-3.154711	-0.760111
C	0.909932	-2.296772	2.308413
Cl	-1.565182	1.123246	-2.466611
Cl	-1.304029	1.416595	2.153583
H	1.358396	-0.069635	-0.006728
H	4.602616	3.383859	0.301560
H	3.549077	5.373663	-0.728434
H	1.202812	5.257403	-1.566221
H	-0.064784	3.147602	-1.368760
H	-3.315616	-3.120493	1.383263
H	-3.755244	-3.319712	-0.324062
H	-1.201589	-4.095507	0.847608
H	-1.531815	-3.988961	-0.890299
H	-3.886088	0.098145	3.585704
H	-4.346863	-1.561970	3.186292
H	-2.762410	-0.916783	2.696714
H	-5.921876	0.969164	2.561767
H	-7.946475	1.883751	1.524282
H	-8.242327	1.672438	-0.212307
H	-7.182806	2.965615	0.354996
H	-6.435380	0.730541	-1.686906

H	-4.436119	-2.027243	-2.211583
H	-5.090020	-0.594859	-3.013578
H	-3.380452	-0.647238	-2.565013
H	0.460453	-1.305343	2.439077
H	0.132304	-3.035073	2.542313
H	1.704916	-2.409888	3.051501
H	3.470058	-2.822451	1.576259
H	5.423117	-2.236214	-0.644231
H	5.041723	-3.557899	-1.756790
H	5.205047	-3.872877	-0.019963
H	2.909826	-2.864101	-2.674686
H	-0.215855	-1.358992	-2.779933
H	0.833417	-2.488837	-3.654880
H	-0.557835	-3.089738	-2.747870
C	4.744162	0.776804	0.651605
C	5.335046	0.384560	1.853668
C	5.487880	0.821859	-0.531616
C	6.686537	0.036277	1.871243
H	4.728425	0.357820	2.753267
C	6.840923	0.480465	-0.497849
H	5.010554	1.118581	-1.459957
C	7.445051	0.086362	0.699406
H	7.147443	-0.268501	2.806818
H	7.422053	0.517437	-1.415366
H	8.497930	-0.179665	0.717770

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M06 SCF energy: -615.61005856 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.134151	1.860226	0.252953
H	1.175698	2.370005	0.297956
C	2.053402	0.404900	0.049054
C	0.835185	-0.185634	-0.346331
C	0.722693	-1.563274	-0.553438
C	1.829336	-2.384931	-0.354509
C	3.047842	-1.828977	0.046951
C	3.149584	-0.455794	0.243173
H	4.093497	-0.033528	0.574580
H	3.912543	-2.465527	0.211389
H	1.739802	-3.455575	-0.516164
H	-0.227235	-1.978006	-0.874391
O	-0.223429	0.665827	-0.608982
C	3.253170	2.587671	0.367474

H	4.249021	2.158065	0.295082
H	3.204169	3.660145	0.530045
C	-1.509517	0.334977	-0.224185
C	-2.539035	0.744001	-1.075014
C	-1.796361	-0.302412	0.987019
C	-3.865101	0.510331	-0.711273
H	-2.283885	1.241398	-2.005429
C	-3.127778	-0.536756	1.333995
H	-0.989465	-0.606569	1.645537
C	-4.166122	-0.133851	0.491170
H	-4.664532	0.829859	-1.374374
H	-3.351316	-1.031457	2.275505
H	-5.199559	-0.318286	0.769889

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M06 SCF energy: -2402.38745846 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.162994	0.512631	0.022305
C	-0.226296	-1.498061	0.008267
N	0.755153	-2.438201	0.019376
C	0.240868	-3.821143	-0.030194
C	-1.265791	-3.624670	0.166024
N	-1.416878	-2.165930	0.023617
H	-1.603807	-3.942609	1.159874
H	-1.866983	-4.148870	-0.582583
H	0.700363	-4.426960	0.756574
H	0.484262	-4.279729	-0.996419
C	-2.739704	-1.596723	0.039634
C	-3.424428	-1.437204	-1.186685
C	-4.708585	-0.889057	-1.160031
C	-5.339168	-0.531627	0.037611
C	-4.670901	-0.789785	1.234957
C	-3.384667	-1.344219	1.266568
H	-5.234959	-0.749670	-2.101866
H	-5.164104	-0.570576	2.179760
C	-2.793630	-1.742181	2.598214
H	-3.166297	-2.735066	2.890136
H	-1.704900	-1.765378	2.584338
H	-3.089471	-1.037932	3.380645
C	-2.831230	-1.899893	-2.495580
H	-3.534684	-1.721625	-3.314666
H	-2.615594	-2.976571	-2.476297
H	-1.902804	-1.371620	-2.725772

C	-6.709996	0.103456	0.029293
H	-7.212897	-0.013611	0.994872
H	-7.350883	-0.334728	-0.744159
H	-6.644768	1.179825	-0.178055
C	2.175540	-2.252806	-0.035979
C	2.816812	-2.178011	-1.286706
C	4.209647	-2.044211	-1.303797
H	4.715653	-1.973330	-2.264391
C	4.291247	-2.071588	1.097125
C	2.900626	-2.207006	1.169056
H	4.860697	-2.023550	2.022930
C	4.964571	-1.992622	-0.126829
C	2.200867	-2.257597	2.506570
H	2.928552	-2.219987	3.322884
H	1.616820	-3.179013	2.626448
H	1.505896	-1.418107	2.627257
H	1.440980	-3.103222	-2.693194
C	2.033780	-2.187219	-2.578628
H	2.709892	-2.124657	-3.436615
H	1.336133	-1.343153	-2.632121
C	6.471245	-1.882870	-0.177379
H	6.804452	-1.340526	-1.068653
H	6.939588	-2.875891	-0.207956
H	6.866117	-1.365897	0.703698
Cl	-0.632847	0.763021	-2.331758
Cl	-0.500785	0.686234	2.398591
C	1.649342	0.862906	-0.023233
H	2.424378	0.101216	-0.084213
C	2.124036	2.228079	0.032509
C	1.182500	3.281006	0.103248
C	1.579400	4.610878	0.204170
C	2.947514	4.901240	0.218049
C	3.904931	3.884873	0.134184
C	3.493084	2.558794	0.042667
H	4.221874	1.754288	-0.013913
H	4.962634	4.130344	0.144957
H	3.264409	5.937952	0.293177
H	0.845067	5.405200	0.260868
O	-0.116394	2.852987	0.056601
C	-1.168899	3.763117	0.332096
C	-1.666888	4.639177	-0.785649
C	-2.478983	3.452003	-0.309657
H	-1.138026	4.132683	1.353852
H	-1.173013	4.534988	-1.747092
H	-1.995086	5.646168	-0.540440
H	-3.374275	3.622178	0.281066
H	-2.509564	2.587156	-0.965606

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M06 SCF energy: -2402.36673478 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.816212	2.466246	0.982911
C	-0.998974	2.425997	-0.162431
C	-1.521539	2.650960	-1.449026
C	-2.892678	2.905872	-1.563511
C	-3.735967	2.954287	-0.449262
C	-3.179034	2.729252	0.813848
N	0.412679	2.235234	0.011169
C	1.141198	1.087739	-0.011023
N	2.446822	1.426145	0.197718
C	2.631977	2.858761	0.482632
C	1.250663	3.441684	0.163837
Ru	0.632291	-0.792589	-0.327431
C	-1.214114	-0.723887	-0.358054
C	-2.019095	-1.875956	-0.724769
C	-1.556993	-2.877367	-1.608279
C	-2.342547	-3.976317	-1.937780
C	-3.616935	-4.101437	-1.381461
C	-4.112553	-3.134271	-0.504700
C	-3.326536	-2.027653	-0.174597
O	-3.732101	-1.047792	0.684799
C	3.564367	0.528418	0.346244
C	3.905198	0.045498	1.625675
C	5.001305	-0.816466	1.734448
C	5.776386	-1.174855	0.629342
C	5.463187	-0.606016	-0.609494
C	4.377832	0.258848	-0.775539
C	3.189407	0.488911	2.879846
C	6.922764	-2.148678	0.767703
C	4.142100	0.924243	-2.110063
C	-0.649458	2.599707	-2.680743
C	-5.206346	3.266770	-0.603823
C	-1.253036	2.186684	2.357149
Cl	1.116498	-0.795455	-2.672039
Cl	0.841002	-1.663601	1.883032
H	-1.765863	0.127041	0.032475
H	-5.097743	-3.251526	-0.069872
H	-4.238910	-4.957681	-1.629265
H	-1.968143	-4.724360	-2.629801
H	-0.584196	-2.748316	-2.072481

H	2.914465	2.999558	1.532956
H	3.426292	3.275283	-0.143735
H	0.858780	4.077629	0.963290
H	1.243949	4.022718	-0.766096
H	3.216041	-0.298532	3.637493
H	3.682714	1.374783	3.306437
H	2.140898	0.726907	2.700543
H	5.254836	-1.213306	2.715141
H	7.349890	-2.126017	1.775940
H	7.723436	-1.931787	0.052217
H	6.587601	-3.177118	0.578819
H	6.086099	-0.831241	-1.472357
H	4.207200	2.017373	-2.025909
H	4.900154	0.605673	-2.831947
H	3.159447	0.678116	-2.519923
H	-0.837937	1.173596	2.421237
H	-0.445995	2.881395	2.621670
H	-2.032574	2.282861	3.119097
H	-3.821095	2.751398	1.691683
H	-5.590646	2.917511	-1.568029
H	-5.389637	4.348600	-0.553517
H	-5.800383	2.799612	0.188817
H	-3.310605	3.069703	-2.554522
H	-0.161284	1.625061	-2.789094
H	-1.245913	2.783862	-3.579337
H	0.142808	3.358714	-2.652227
C	-5.022973	-1.125679	1.238906
C	-5.234227	-1.972982	2.465357
C	-5.182041	-0.461631	2.568625
H	-5.821837	-1.044060	0.502581
H	-4.374235	-2.525562	2.831708
H	-6.189186	-2.477157	2.588827
H	-6.100391	0.085073	2.763633
H	-4.286765	-0.025351	3.001230

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M06 SCF energy: -501.32177118 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.376031	1.884053	-0.133685
H	-0.492649	2.379003	-0.527863
C	-1.296610	0.414953	-0.078858
C	-0.036379	-0.226271	-0.155731
C	0.064139	-1.620257	-0.111654

C	-1.089317	-2.397386	0.006966
C	-2.342762	-1.789475	0.076830
C	-2.433791	-0.399950	0.029365
H	-3.411505	0.072436	0.055039
H	-3.243207	-2.391639	0.156718
H	-1.001014	-3.480066	0.039912
H	1.036626	-2.095894	-0.155081
O	1.052192	0.603691	-0.268306
C	-2.409392	2.638583	0.263727
H	-3.309182	2.220225	0.707660
H	-2.380195	3.719675	0.164886
C	2.318907	0.028420	-0.461789
C	3.472389	0.872584	-0.025220
C	3.122537	-0.387088	0.742869
H	2.403566	-0.551919	-1.380319
H	3.228763	1.823294	0.439665
H	4.365503	0.882216	-0.643481
H	3.774033	-1.253240	0.659979
H	2.649576	-0.262621	1.712409

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M06 SCF energy: -2482.21167815 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.098006	0.251192	-0.063450
C	-0.426729	-1.685850	0.011549
N	-1.635978	-2.304022	0.062868
C	-1.538597	-3.777572	0.054491
C	-0.034739	-4.016284	0.224433
N	0.523509	-2.665838	0.038143
H	0.375095	-4.707967	-0.517525
H	0.220599	-4.394128	1.221974
H	-1.923630	-4.174857	-0.892410
H	-2.134749	-4.203005	0.867418
C	1.954042	-2.494288	0.037441
C	2.652916	-2.401377	1.257875
C	4.042990	-2.235882	1.213063
C	4.749244	-2.209985	0.009575
C	4.035312	-2.407487	-1.177946
C	2.647847	-2.570584	-1.191482
H	4.584277	-2.139844	2.152040
H	4.573934	-2.451295	-2.122148
C	1.942045	-2.890514	-2.486891
H	1.435936	-3.863665	-2.433552

H	1.195553	-2.133165	-2.736848
H	2.662516	-2.941155	-3.308968
C	1.982036	-2.578251	2.599482
H	2.449417	-1.941543	3.355592
H	2.087345	-3.620719	2.934099
H	0.924034	-2.321433	2.575945
C	6.243440	-1.987506	-0.013266
H	6.719893	-2.543923	-0.827972
H	6.709874	-2.295257	0.928564
H	6.480868	-0.925940	-0.163468
C	-2.946764	-1.723125	0.032965
C	-3.591208	-1.442876	1.252316
C	-4.887734	-0.919297	1.207641
H	-5.391159	-0.688408	2.144110
C	-4.878429	-0.979949	-1.193994
C	-3.581215	-1.504297	-1.204424
H	-5.374850	-0.795941	-2.144478
C	-5.549466	-0.683992	-0.002454
C	-2.877435	-1.776497	-2.513114
H	-3.539782	-1.559403	-3.356579
H	-2.565344	-2.824608	-2.601063
H	-1.975873	-1.162037	-2.620075
H	-2.570688	-2.697501	2.702073
C	-2.894699	-1.656753	2.575347
H	-3.565052	-1.415925	3.406010
H	-1.999818	-1.029100	2.663305
C	-6.964551	-0.152919	-0.021649
H	-7.169601	0.475439	0.851623
H	-7.695148	-0.972958	-0.009979
H	-7.158601	0.440386	-0.921557
Cl	0.489862	0.385585	2.312644
Cl	0.495594	0.254741	-2.450191
C	-1.532726	1.106984	-0.057975
H	-2.494855	0.597784	-0.057284
C	-1.594063	2.550147	-0.029467
C	-0.396222	3.301672	-0.098934
C	-0.429227	4.695632	-0.082540
C	-1.662020	5.348241	0.003776
C	-2.859239	4.628926	0.076283
C	-2.820171	3.239601	0.061249
H	-3.737035	2.658104	0.115374
H	-3.808357	5.151800	0.145376
H	-1.680586	6.434592	0.022071
H	0.485129	5.274823	-0.113249
O	0.745676	2.547489	-0.156986
C	1.922657	3.038815	-0.865221
H	2.111199	2.288318	-1.637162

H	1.655725	3.977349	-1.358679
C	3.154201	3.217929	0.039544
C	2.870880	4.204816	1.186009
C	3.599247	1.862882	0.621028
C	4.269348	3.779085	-0.867667
H	2.620342	5.204327	0.807317
H	2.047205	3.854557	1.816444
H	3.757273	4.309972	1.822528
H	3.800311	1.135535	-0.175292
H	4.522012	1.987957	1.201527
H	2.838421	1.441686	1.284624
H	5.191884	3.915257	-0.291861
H	4.491763	3.097410	-1.697739
H	3.995575	4.752938	-1.293514

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M06 SCF energy: -2482.18937919 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-0.922564	-0.706854	0.542700
C	-1.505486	1.068320	-0.086050
N	-0.863650	2.266934	-0.136707
C	-1.727656	3.354775	-0.639233
C	-3.116667	2.709350	-0.638637
N	-2.801169	1.282713	-0.456678
H	-3.742381	3.065033	0.188918
H	-3.663327	2.864860	-1.573238
H	-1.405456	3.660246	-1.642520
H	-1.659561	4.226057	0.018278
Cl	-0.919692	-1.975416	-1.477288
Cl	-1.597061	-0.329306	2.807703
C	-3.843945	0.300369	-0.607232
C	-4.036193	-0.282561	-1.878773
C	-5.060094	-1.219304	-2.028008
C	-5.902294	-1.572527	-0.967679
C	-5.734823	-0.917200	0.253296
C	-4.731738	0.039580	0.455103
C	-4.700045	0.812073	1.752799
H	-3.687915	1.072226	2.064174
H	-5.287042	1.737440	1.659470
H	-5.148091	0.225906	2.560590
H	-6.410796	-1.141465	1.075676
C	-6.965200	-2.631063	-1.145045
H	-6.540463	-3.636364	-1.024787

H	-7.412992	-2.587171	-2.144172
H	-7.766584	-2.523761	-0.406610
H	-5.203870	-1.684279	-3.000801
C	-3.193458	0.110448	-3.068112
H	-2.162461	-0.234474	-2.950867
H	-3.596068	-0.335952	-3.982432
H	-3.173805	1.198463	-3.209896
C	0.525332	2.568883	0.059431
C	1.409342	2.472193	-1.030907
C	2.737685	2.869671	-0.839887
C	3.196687	3.350894	0.389980
C	2.287554	3.434141	1.450055
C	0.948771	3.055280	1.310448
C	-0.003935	3.160007	2.476858
H	-0.433536	2.184885	2.731448
H	0.511647	3.550129	3.359568
H	-0.842077	3.834801	2.259156
C	0.961411	1.918936	-2.364121
H	0.584442	0.894080	-2.266591
H	0.157286	2.516014	-2.811538
H	1.793987	1.905199	-3.073417
H	3.428420	2.801826	-1.677690
H	2.626039	3.808061	2.414092
C	4.641311	3.753412	0.579074
H	5.210647	2.963152	1.086540
H	4.728872	4.656158	1.193923
H	5.132235	3.948655	-0.380018
C	0.910600	-0.517583	0.689606
H	1.448576	0.285450	0.192312
C	1.742621	-1.530364	1.314674
C	1.258838	-2.385782	2.330552
C	2.072401	-3.342649	2.924942
C	3.396773	-3.471940	2.501927
C	3.912184	-2.651810	1.497015
C	3.101541	-1.681507	0.899207
H	4.934525	-2.796425	1.170308
H	4.042340	-4.222056	2.951388
H	1.681230	-3.976770	3.714460
H	0.242018	-2.244347	2.683191
O	3.499597	-0.861736	-0.110225
C	4.878501	-0.652287	-0.439911
H	5.532132	-1.050482	0.342931
H	5.005518	0.436941	-0.455998
C	5.251537	-1.230564	-1.820071
C	5.110865	-2.763494	-1.832839
C	4.338163	-0.618907	-2.898981
C	6.717089	-0.840145	-2.093249

H	5.784426	-3.235286	-1.106446
H	4.086489	-3.073363	-1.601864
H	5.364493	-3.160510	-2.822864
H	4.431314	0.474542	-2.921317
H	4.608274	-0.997870	-3.891605
H	3.288691	-0.866446	-2.712891
H	7.037006	-1.213889	-3.072569
H	6.849770	0.249097	-2.094115
H	7.394605	-1.261975	-1.339922

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M06 SCF energy: -581.14745123 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.606239	1.954203	0.142497
H	0.597173	2.193208	0.467003
C	1.919176	0.517369	0.072941
C	0.868257	-0.433509	0.019086
C	1.150267	-1.803156	-0.043277
C	2.475225	-2.244408	-0.052554
C	3.523044	-1.327152	0.007394
C	3.235829	0.035047	0.075022
H	4.050347	0.749447	0.152207
H	4.554404	-1.667667	0.014084
H	2.679918	-3.310679	-0.099746
H	0.347017	-2.528953	-0.087703
O	-0.400277	0.075153	0.023369
C	-1.510338	-0.817080	-0.026361
H	-1.455230	-1.422183	-0.943446
H	-1.476126	-1.499922	0.835610
C	2.433997	2.961985	-0.164805
H	3.442906	2.802796	-0.537039
H	2.116606	3.995447	-0.061696
C	-2.817774	-0.008446	-0.007872
C	-2.914083	0.809732	1.293513
C	-2.872554	0.929555	-1.228281
C	-3.981470	-1.016379	-0.073088
H	-2.885431	0.156625	2.174780
H	-2.087499	1.521983	1.375386
H	-3.854251	1.372972	1.324976
H	-2.823974	0.361443	-2.165800
H	-3.807566	1.502267	-1.232202
H	-2.037733	1.636692	-1.219754
H	-4.943147	-0.490669	-0.063005

H	-3.941608	-1.618616	-0.989388
H	-3.968480	-1.701979	0.783483

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M06 SCF energy: -2675.07694967 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.254098	0.048406	0.066271
C	1.367861	-1.615732	0.029376
N	2.712750	-1.811946	-0.019127
C	3.097611	-3.235612	0.053160
C	1.752789	-3.954897	-0.082119
N	0.786491	-2.851659	0.058369
H	1.591147	-4.708828	0.693891
H	1.631217	-4.438895	-1.058861
H	3.591465	-3.442813	1.010084
H	3.798475	-3.480957	-0.750418
C	-0.619215	-3.167666	0.067059
C	-1.298264	-3.383847	-1.149390
C	-2.658309	-3.713590	-1.098728
C	-3.338918	-3.877901	0.108833
C	-2.611448	-3.749132	1.297203
C	-1.254270	-3.415928	1.305033
H	-3.191006	-3.860207	-2.036191
H	-3.108096	-3.928964	2.248260
C	-0.495665	-3.397013	2.609778
H	0.334417	-4.115781	2.598565
H	-0.081207	-2.408181	2.821805
H	-1.157197	-3.674060	3.436343
C	-0.602743	-3.374979	-2.490304
H	-1.252019	-2.951189	-3.261334
H	-0.359846	-4.404428	-2.791681
H	0.312142	-2.784210	-2.485452
C	-4.815842	-4.195038	0.134459
H	-5.076784	-4.823584	0.992919
H	-5.131345	-4.713779	-0.776978
H	-5.414354	-3.277324	0.210596
C	3.771956	-0.846065	-0.069758
C	4.261989	-0.446314	-1.327664
C	5.328393	0.458516	-1.363134
H	5.706920	0.783047	-2.330138
C	5.405428	0.530509	1.036580
C	4.340946	-0.373338	1.127568
H	5.845237	0.912232	1.955576

C	5.915337	0.956448	-0.194596
C	3.804153	-0.786820	2.477328
H	4.371528	-0.304017	3.278735
H	3.876415	-1.870919	2.631502
H	2.749136	-0.513355	2.592871
H	3.647263	-2.032482	-2.679577
C	3.631191	-0.937473	-2.609281
H	4.168636	-0.543384	-3.477117
H	2.582325	-0.626396	-2.685886
C	7.090594	1.904667	-0.260768
H	7.054372	2.527187	-1.161169
H	8.041231	1.355061	-0.284454
H	7.121319	2.567303	0.610634
Cl	-0.221173	-0.069589	-2.304242
Cl	0.019013	0.050487	2.473533
C	1.532593	1.366432	-0.061114
H	2.593489	1.174466	-0.209026
C	1.175375	2.760598	0.027507
C	-0.180696	3.154217	0.173548
C	-0.499977	4.506788	0.330385
C	0.517973	5.463857	0.320909
C	1.856844	5.099876	0.154737
C	2.174769	3.755663	0.009546
H	3.208529	3.440596	-0.107489
H	2.635695	5.856208	0.144248
H	0.251024	6.510451	0.440987
H	-1.524242	4.832578	0.451290
O	-1.085289	2.130533	0.151349
C	-2.482786	2.422430	0.486670
H	-2.444623	3.147691	1.307572
C	-3.188196	1.158048	1.003675
C	-3.262679	3.007660	-0.709573
H	-2.590270	0.731123	1.814629
C	-3.400742	0.118423	-0.115063
C	-4.570929	1.609935	1.535408
H	-2.728766	3.873089	-1.118296
C	-3.448779	1.951743	-1.818454
C	-4.643698	3.454024	-0.174179
H	-3.917543	-0.754367	0.305405
H	-2.444369	-0.242644	-0.508156
C	-4.221601	0.738361	-1.261897
H	-4.449439	2.331758	2.355286
H	-5.095537	0.741270	1.954412
C	-5.399982	2.234086	0.392323
H	-2.476152	1.629814	-2.205616
H	-4.000770	2.405766	-2.653160
H	-4.525974	4.222404	0.603902

H	-5.218428	3.913853	-0.989140
H	-4.356817	-0.004243	-2.058496
C	-5.596568	1.191948	-0.728964
H	-6.376679	2.554960	0.778569
H	-6.196503	1.624140	-1.542462
H	-6.156983	0.328547	-0.342935

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M06 SCF energy: -2675.05847439 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-1.357944	-0.166608	0.949247
C	-2.100428	0.835793	-0.581534
N	-1.665956	1.964962	-1.204610
C	-2.613526	2.453573	-2.226903
C	-3.846554	1.572430	-1.996941
N	-3.334681	0.539897	-1.079444
H	-4.669424	2.121211	-1.524122
H	-4.224169	1.113321	-2.915496
H	-2.186555	2.329130	-3.229500
H	-2.815707	3.517891	-2.075839
Cl	-0.878044	-2.325951	0.052396
Cl	-2.469373	1.255271	2.526379
C	-4.142433	-0.619220	-0.798011
C	-3.957395	-1.771084	-1.592388
C	-4.758855	-2.885035	-1.338022
C	-5.739568	-2.880236	-0.340055
C	-5.943738	-1.700646	0.377973
C	-5.176304	-0.550051	0.155993
C	-5.533107	0.728595	0.876020
H	-4.655132	1.324337	1.129622
H	-6.205225	1.342815	0.259304
H	-6.063027	0.510068	1.808077
H	-6.731617	-1.662172	1.127228
C	-6.553259	-4.119709	-0.051357
H	-6.011620	-4.794812	0.624179
H	-6.766853	-4.682116	-0.967168
H	-7.506447	-3.872818	0.427792
H	-4.612262	-3.781353	-1.936695
C	-2.943843	-1.810383	-2.710663
H	-1.924799	-1.823754	-2.313038
H	-3.080613	-2.712150	-3.315171
H	-3.036797	-0.944135	-3.377561
C	-0.376999	2.595289	-1.146273

C	0.643550	2.136416	-2.001121
C	1.867237	2.813830	-1.994205
C	2.093168	3.922414	-1.171621
C	1.049849	4.361014	-0.351034
C	-0.194491	3.721262	-0.323241
C	-1.297783	4.236547	0.568535
H	-1.621628	3.476024	1.286634
H	-0.961372	5.116741	1.124709
H	-2.183364	4.530564	-0.009787
C	0.444382	0.929233	-2.888795
H	0.218538	0.030263	-2.303486
H	-0.383823	1.067527	-3.594545
H	1.345851	0.730729	-3.475261
H	2.661898	2.466753	-2.651210
H	1.203445	5.229123	0.286392
C	3.435691	4.615672	-1.154883
H	4.085078	4.198462	-0.373717
H	3.331809	5.686791	-0.950907
H	3.959225	4.500458	-2.109976
C	0.392902	0.419465	1.012497
H	0.896569	0.788152	0.120585
C	1.246453	0.213522	2.172576
C	0.753963	0.298855	3.493471
C	1.591351	0.152585	4.594126
C	2.950048	-0.090354	4.391972
C	3.474234	-0.198014	3.102294
C	2.637781	-0.060286	1.988555
H	4.530815	-0.399492	2.977563
H	3.617956	-0.202855	5.242171
H	1.189061	0.238101	5.598894
H	-0.295542	0.533191	3.635733
O	3.053789	-0.179428	0.700943
C	4.404487	-0.577329	0.395133
H	5.090859	0.022955	1.008868
C	4.654465	-0.250380	-1.088206
C	4.641745	-2.084011	0.643075
H	4.449939	0.816166	-1.246893
C	3.740204	-1.105272	-1.990810
C	6.133040	-0.564748	-1.405877
H	4.436008	-2.322325	1.692603
C	3.721583	-2.925215	-0.266588
C	6.121248	-2.390455	0.321037
H	3.928460	-0.849416	-3.043281
H	2.688971	-0.879420	-1.783596
C	4.017597	-2.602851	-1.745453
H	6.798100	0.052469	-0.785320
H	6.344274	-0.306198	-2.452125

C	6.412894	-2.062512	-1.157914
H	2.668684	-2.723762	-0.037062
H	3.895066	-3.991337	-0.067396
H	6.785402	-1.807705	0.975598
H	6.326789	-3.449927	0.523166
H	3.365753	-3.206615	-2.389555
C	5.495850	-2.913861	-2.061579
H	7.464971	-2.281367	-1.383219
H	5.699631	-3.981877	-1.902232
H	5.709967	-2.702971	-3.118840

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M06 SCF energy: -774.01260241 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.721008	1.940678	0.065691
H	-1.707721	2.298762	0.224144
C	-2.870117	0.476254	0.035217
C	-1.730736	-0.345664	-0.165988
C	-1.862628	-1.739893	-0.195258
C	-3.117107	-2.330077	-0.031535
C	-4.247145	-1.539906	0.173757
C	-4.110790	-0.154037	0.211174
H	-4.984528	0.463215	0.399039
H	-5.222007	-1.996890	0.316737
H	-3.200705	-3.413413	-0.055552
H	-0.996690	-2.373658	-0.343169
O	-0.547347	0.316597	-0.342857
C	-3.698003	2.843477	-0.095517
H	-4.729318	2.567539	-0.300537
H	-3.488039	3.907421	-0.037379
C	0.675963	-0.398834	-0.575693
H	0.470964	-1.228429	-1.266063
C	1.301338	-0.934334	0.731516
C	1.654077	0.576819	-1.256795
H	0.592150	-1.607718	1.227625
C	1.644504	0.239956	1.672598
C	2.589995	-1.705398	0.369001
H	1.180006	0.962261	-2.167833
C	2.001557	1.742929	-0.308064
C	2.940587	-0.200030	-1.612878
H	2.074536	-0.153580	2.603700
H	0.730894	0.781672	1.944185
C	2.644562	1.190079	0.980954

H	2.355817	-2.554807	-0.288502
H	3.035844	-2.124912	1.280820
C	3.587201	-0.755077	-0.326036
H	1.098116	2.315301	-0.068541
H	2.693312	2.430368	-0.814038
H	2.711768	-1.021371	-2.306502
H	3.640128	0.468025	-2.132822
H	2.890913	2.020254	1.655856
C	3.929503	0.413052	0.623175
H	4.502361	-1.305114	-0.581748
H	4.656214	1.084568	0.145130
H	4.404242	0.027758	1.536398

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M06 SCF energy: -2675.07892060 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.283768	0.029869	0.031954
C	1.511400	-1.557896	0.069610
N	2.865793	-1.665503	0.102336
C	3.342237	-3.058932	0.205893
C	2.052469	-3.870588	0.043148
N	1.011270	-2.829584	0.089504
H	1.903213	-4.599684	0.845365
H	2.010287	-4.404005	-0.913937
H	3.822572	-3.221450	1.177874
H	4.080528	-3.266846	-0.574939
C	-0.369676	-3.227480	-0.010544
C	-0.929175	-3.495621	-1.277253
C	-2.271576	-3.885988	-1.338731
C	-3.048446	-4.057795	-0.190679
C	-2.434260	-3.878181	1.052937
C	-1.097262	-3.485348	1.172060
H	-2.713548	-4.072662	-2.315380
H	-3.004044	-4.066211	1.960455
C	-0.455011	-3.415636	2.536269
H	0.395410	-4.106530	2.609949
H	-0.090547	-2.410371	2.762740
H	-1.175400	-3.700005	3.309531
C	-0.114346	-3.472403	-2.548881
H	-0.734392	-3.180578	-3.400808
H	0.283178	-4.476245	-2.759235
H	0.715411	-2.768397	-2.499868
C	-4.507283	-4.439307	-0.289090

H	-4.836180	-4.999252	0.592898
H	-4.703621	-5.052435	-1.175358
H	-5.144431	-3.547756	-0.364780
C	3.854415	-0.627210	0.074717
C	4.352009	-0.199510	-1.170455
C	5.354103	0.776799	-1.180541
H	5.738427	1.122090	-2.138016
C	5.352852	0.866291	1.219966
C	4.350550	-0.107817	1.285119
H	5.736200	1.283122	2.148983
C	5.870347	1.318966	0.001361
C	3.797481	-0.548148	2.619718
H	4.299525	-0.019208	3.435508
H	3.941675	-1.623024	2.787604
H	2.721794	-0.350625	2.694039
H	3.899532	-1.830455	-2.532517
C	3.794367	-0.740026	-2.466072
H	4.320180	-0.305514	-3.321658
H	2.726477	-0.512869	-2.569624
C	6.980282	2.344292	-0.035427
H	6.965825	2.918453	-0.967824
H	7.965248	1.863429	0.035349
H	6.904370	3.048924	0.799775
Cl	-0.187517	-0.152968	-2.332358
Cl	-0.020609	0.046311	2.438479
C	1.463105	1.439028	-0.073014
H	2.546963	1.338728	-0.090564
C	0.969564	2.792853	-0.145020
C	-0.429714	3.045173	-0.118546
C	-0.893358	4.362030	-0.197463
C	0.020515	5.414419	-0.299519
C	1.398542	5.185939	-0.324130
C	1.861973	3.879066	-0.246377
H	2.927944	3.666721	-0.263640
H	2.093658	6.016219	-0.403050
H	-0.361902	6.429958	-0.359764
H	-1.948105	4.589309	-0.181175
O	-1.183617	1.911753	-0.009330
C	-2.663267	1.850603	0.034787
C	-3.216834	2.571499	1.278351
C	-3.285542	2.378847	-1.271213
C	-2.987450	0.350058	0.158656
H	-2.978502	3.638881	1.270146
H	-2.747560	2.143154	2.171720
C	-4.753199	2.387969	1.317812
H	-2.859785	1.821399	-2.113569
H	-3.054483	3.435642	-1.434176

C	-4.820630	2.195407	-1.201802
H	-2.518274	-0.045910	1.065858
H	-2.568756	-0.181814	-0.702766
C	-4.517748	0.145022	0.215090
H	-5.149294	2.929323	2.186534
C	-5.374254	2.955792	0.022993
C	-5.091539	0.889379	1.436562
H	-5.264570	2.599840	-2.120502
C	-5.156952	0.696906	-1.074033
H	-4.720311	-0.929891	0.303414
H	-5.151580	4.028715	-0.065100
H	-6.467922	2.860552	0.059930
H	-4.669240	0.479524	2.363501
H	-6.180378	0.751393	1.488756
H	-6.246383	0.555639	-1.049138
H	-4.779479	0.150540	-1.948352

12-B

M06 SCF energy: -2675.06001669 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	-1.262214	-0.235075	0.888346
C	-2.005044	0.897284	-0.550730
N	-1.556604	2.049430	-1.114984
C	-2.508787	2.614108	-2.093316
C	-3.759086	1.752046	-1.888061
N	-3.254557	0.656916	-1.042359
H	-4.166349	1.355961	-2.823095
H	-4.558245	2.292518	-1.367135
H	-2.101050	2.531439	-3.108070
H	-2.680762	3.673657	-1.882997
C	-4.097050	-0.481857	-0.780813
C	-5.092525	-0.414252	0.213712
C	-5.891295	-1.546063	0.421519
C	-5.757378	-2.701991	-0.349364
C	-4.820034	-2.698483	-1.388487
C	-3.990103	-1.603100	-1.631585
H	-6.648263	-1.510626	1.202127
H	-4.732030	-3.572570	-2.029972
C	-3.033886	-1.624523	-2.799967
H	-3.143150	-0.733880	-3.431391
H	-1.996317	-1.671388	-2.457423
H	-3.221091	-2.501643	-3.426759
C	-5.385593	0.849177	0.987468

H	-5.864018	0.614286	1.942989
H	-6.082276	1.487855	0.425156
H	-4.485826	1.424992	1.206077
C	-6.602182	-3.923783	-0.075129
H	-6.888595	-4.431092	-1.003184
H	-7.516717	-3.666218	0.469190
H	-6.051108	-4.651699	0.534719
C	-0.267234	2.673449	-1.016979
C	-0.083175	3.735916	-0.114775
C	1.158649	4.382277	-0.106024
H	1.315763	5.199836	0.594116
C	1.964547	2.968646	-1.870579
C	0.747067	2.283826	-1.912976
H	2.754871	2.676377	-2.558328
C	2.194328	4.012851	-0.967858
C	0.545962	1.139346	-2.880084
H	1.450005	0.974649	-3.473787
H	-0.275391	1.329531	-3.581853
H	0.309003	0.205935	-2.356245
H	-2.072237	4.512105	0.270890
C	-1.182204	4.178303	0.820307
H	-0.845282	5.015197	1.439444
H	-1.499013	3.365298	1.481809
C	3.537099	4.702585	-0.912674
H	3.459272	5.698343	-0.464227
H	3.974506	4.812047	-1.911321
H	4.247842	4.124129	-0.307991
Cl	-2.309426	1.062751	2.604168
Cl	-0.854518	-2.322122	-0.191361
C	0.498793	0.324307	1.010978
H	1.005407	0.817452	0.182791
C	1.347764	0.005611	2.150081
C	2.768427	-0.003688	2.012399
C	3.576777	-0.191602	3.138487
C	3.010879	-0.439509	4.388674
C	1.622215	-0.482379	4.535456
C	0.807690	-0.249079	3.434745
H	-0.267993	-0.203216	3.566751
H	1.176989	-0.663737	5.509205
H	3.657759	-0.585524	5.249863
H	4.652591	-0.124313	3.026982
O	3.330951	0.263504	0.792508
C	3.952348	-0.801598	-0.001368
C	5.225726	-1.365084	0.658900
C	2.970336	-1.949565	-0.285663
C	4.332195	-0.107052	-1.317335
H	4.974093	-1.863491	1.601614

H	5.914594	-0.541489	0.890306
C	5.896160	-2.381455	-0.294626
H	2.048170	-1.558577	-0.730260
H	2.681074	-2.442491	0.650669
C	3.635576	-2.969439	-1.239046
H	5.009707	0.729145	-1.100361
H	3.427373	0.317542	-1.766958
C	4.996250	-1.117786	-2.275004
H	6.800814	-2.776534	0.185824
C	4.911534	-3.533994	-0.581000
C	6.271896	-1.681205	-1.615844
H	2.925659	-3.781771	-1.436267
C	4.010614	-2.269847	-2.562109
H	5.257028	-0.608727	-3.212292
H	4.656648	-4.053670	0.352629
H	5.382010	-4.275224	-1.241516
H	6.988564	-0.870528	-1.424030
H	6.765531	-2.391976	-2.292441
H	4.464981	-2.990710	-3.255531
H	3.106912	-1.881440	-3.051299

12-D

M06 SCF energy: -774.01335330 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.289356	1.962228	-0.408327
H	1.548312	2.136229	-1.184462
C	2.611842	0.545244	-0.169362
C	1.711958	-0.466708	-0.579890
C	2.044905	-1.816913	-0.420290
C	3.248476	-2.182673	0.180783
C	4.138873	-1.195655	0.610547
C	3.824481	0.146735	0.420746
H	4.540687	0.910211	0.711135
H	5.085671	-1.471619	1.066502
H	3.496068	-3.234376	0.297355
H	1.360117	-2.571621	-0.791531
O	0.548051	-0.110562	-1.225826
C	2.812454	3.015351	0.234056
H	3.526629	2.912499	1.047359
H	2.528998	4.029537	-0.031903
C	-0.726581	-0.100349	-0.517229
C	-0.638278	0.595727	0.853048
C	-1.665362	0.695283	-1.438719

C	-1.286283	-1.524860	-0.331053
H	-0.217778	1.600844	0.733073
H	0.039006	0.039622	1.513365
C	-2.047931	0.672569	1.482707
H	-1.698568	0.208083	-2.421587
H	-1.251290	1.700197	-1.589871
C	-3.074768	0.775529	-0.816402
H	-0.622118	-2.106578	0.319356
H	-1.319582	-2.028769	-1.305963
C	-2.698088	-1.452376	0.295932
H	-1.976309	1.171332	2.457921
C	-2.984198	1.475570	0.555828
C	-2.608285	-0.752413	1.668046
H	-3.732169	1.348639	-1.482962
C	-3.633877	-0.650155	-0.631454
H	-3.086918	-2.471096	0.423556
H	-2.605905	2.499714	0.432934
H	-3.983013	1.555214	1.006303
H	-1.960956	-1.327998	2.343959
H	-3.601720	-0.710165	2.135125
H	-4.643994	-0.607169	-0.201517
H	-3.721737	-1.151032	-1.605344

C

M06 SCF energy: -2211.97056191 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.386698	0.837894	-0.537314
C	0.772725	-0.938566	0.212287
N	-0.016366	-1.998142	0.537262
C	0.757970	-3.174563	0.979722
C	2.173192	-2.604559	1.141230
N	2.061492	-1.289441	0.489476
H	2.937214	-3.214243	0.649993
H	2.456226	-2.482132	2.193888
H	0.708655	-3.965650	0.221482
H	0.348297	-3.573261	1.912741
C	3.219113	-0.440485	0.371218
C	3.625184	0.346938	1.468243
C	4.757401	1.154368	1.316083
C	5.504881	1.170499	0.136166
C	5.121850	0.313677	-0.900828
C	3.996324	-0.509349	-0.805697
H	5.063725	1.781528	2.150563

H	5.718642	0.276046	-1.809492
C	3.666457	-1.466024	-1.925730
H	3.547156	-2.493121	-1.558192
H	2.738390	-1.182799	-2.431570
H	4.470687	-1.470581	-2.667714
C	2.940073	0.283488	2.812819
H	3.032948	1.237957	3.337673
H	3.409310	-0.486900	3.442207
H	1.875168	0.066154	2.730066
C	6.695532	2.087358	-0.016822
H	7.456958	1.651129	-0.672494
H	7.161241	2.306377	0.949917
H	6.396298	3.046609	-0.459456
C	-1.438547	-2.117971	0.413306
C	-2.240706	-1.792843	1.523770
C	-3.626242	-1.948375	1.405963
H	-4.256411	-1.692842	2.255303
C	-3.389153	-2.732733	-0.853226
C	-1.997681	-2.596399	-0.786596
H	-3.834094	-3.093211	-1.778268
C	-4.219258	-2.420680	0.229293
C	-1.138557	-2.915886	-1.986959
H	-1.753558	-3.294096	-2.809021
H	-0.386866	-3.681449	-1.758775
H	-0.599849	-2.029708	-2.343056
H	-0.887786	-1.923170	3.219200
C	-1.633431	-1.241138	2.792487
H	-2.405589	-1.079064	3.550565
H	-1.126653	-0.285321	2.610820
C	-5.715152	-2.618016	0.140220
H	-6.252359	-1.919866	0.790942
H	-5.997916	-3.633047	0.449664
H	-6.078383	-2.478983	-0.883541
Cl	0.425864	2.122720	1.496378
Cl	0.784197	0.348468	-2.853199
C	-1.452639	0.815632	-0.644396
H	-2.147633	0.102828	-0.188124
O	-2.049908	1.804076	-1.284607
C	-3.494085	1.936706	-1.210775
C	-3.879018	2.983110	-0.172856
H	-3.925023	0.954425	-0.979293
H	-3.806240	2.230311	-2.216611
C	-5.398245	3.194511	-0.100173
H	-3.492483	2.672597	0.806785
H	-3.377909	3.926851	-0.421932
C	-5.797091	4.251686	0.935122
H	-5.774659	3.490912	-1.089423

H	-5.889759	2.241339	0.141806
H	-6.884411	4.382305	0.969239
H	-5.461232	3.968336	1.939692
H	-5.349822	5.224371	0.698638

BVE

M06 SCF energy: -310.91800052 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.148030	0.792761	-0.000092
C	-2.636172	-0.442964	-0.000053
O	-1.333248	-0.820204	0.000057
C	-0.351969	0.215416	0.000135
C	1.024104	-0.436302	0.000042
H	-0.489110	0.850564	-0.887730
H	-0.489077	0.850456	0.888082
H	1.105141	-1.087468	0.880331
H	1.105074	-1.087361	-0.880336
H	-2.546142	1.693920	-0.000068
H	-4.225155	0.914301	-0.000193
H	-3.270487	-1.325931	-0.000130
C	2.163622	0.590841	0.000082
H	2.067587	1.244597	-0.878432
H	2.067714	1.244328	0.878804
C	3.550704	-0.060482	-0.000144
H	4.344721	0.694701	-0.000087
H	3.691157	-0.693191	0.884645
H	3.691000	-0.692901	-0.885165

SUPPLEMENTARY CHARTS

Chart S28: Experimental Ru–O Bond lengths (X-ray, Å) versus computed Ru–O bond strengths, ΔG_r(**A**→**B**) (Method 1, B3YLP).

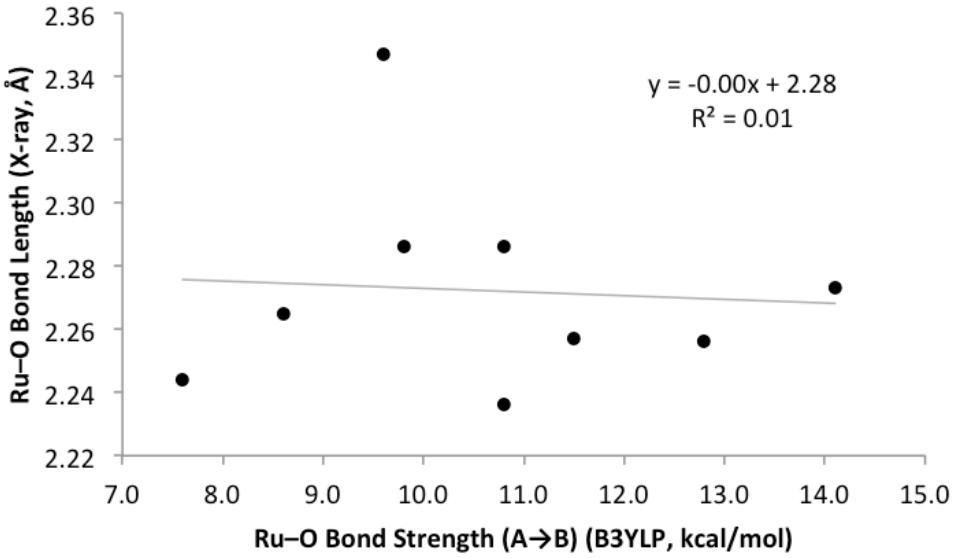


Chart S29: Experimental Ru–O Bond lengths (X-ray, Å) versus computed Ru–O bond strengths, ΔG_r(**A**→**C**) (Method 2, B3YLP).

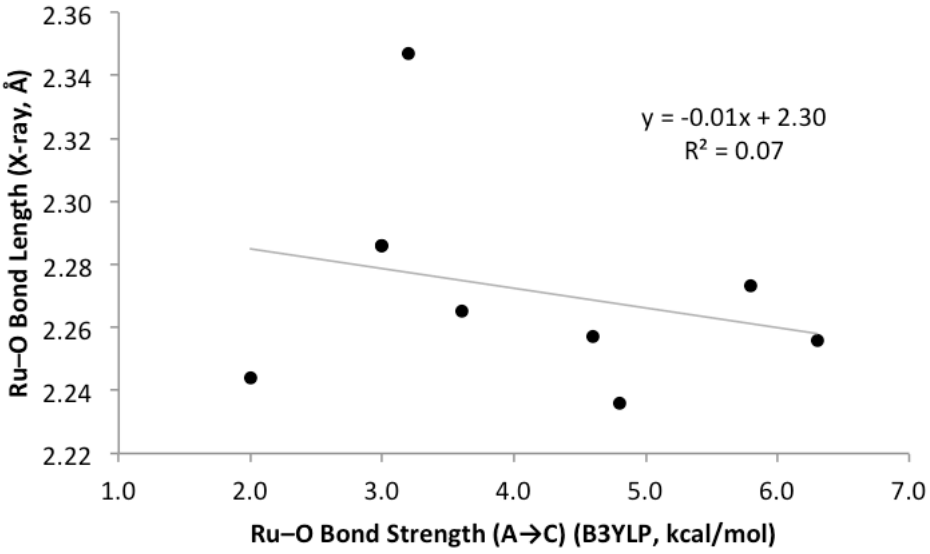


Chart S30: ln(k_{init}) versus experimental Ru–O Bond lengths (X-ray, Å)

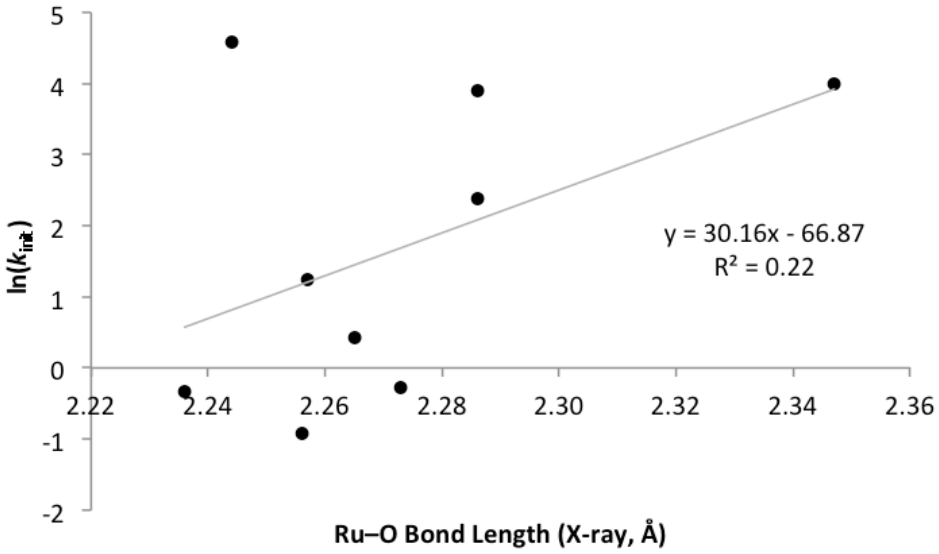


Chart S31: ln(k_{init}) versus NHC ^{13}C NMR shift.

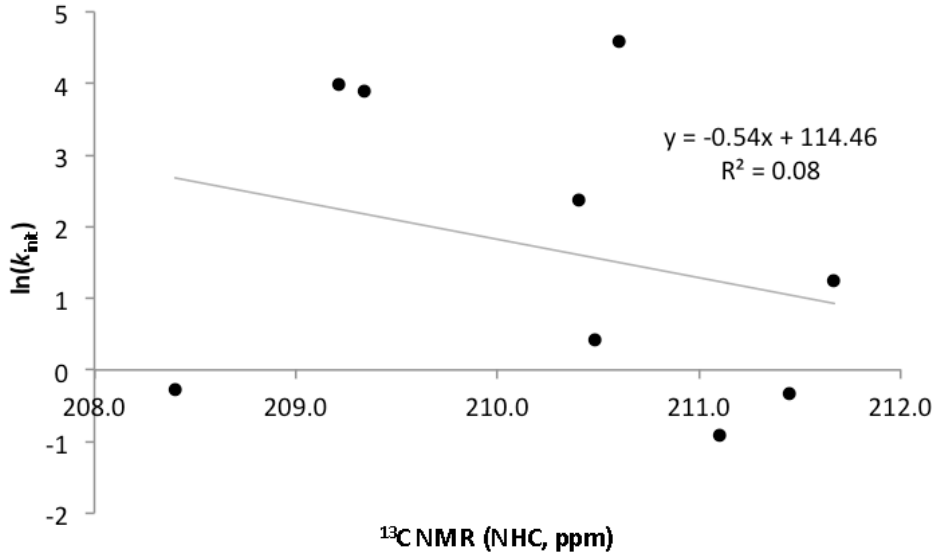


Chart S32: ln(k_{init}) versus NHC ^{13}C NMR shift *with catalyst **6** omitted* (see Chart S31 for comparison).

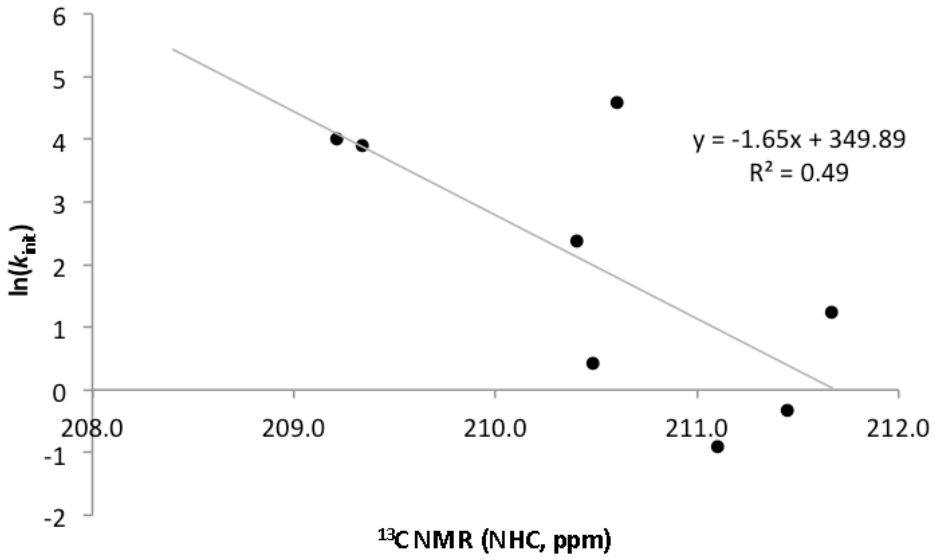


Chart S33: ln(k_{init}) versus benzylidene ^{13}C NMR shift .

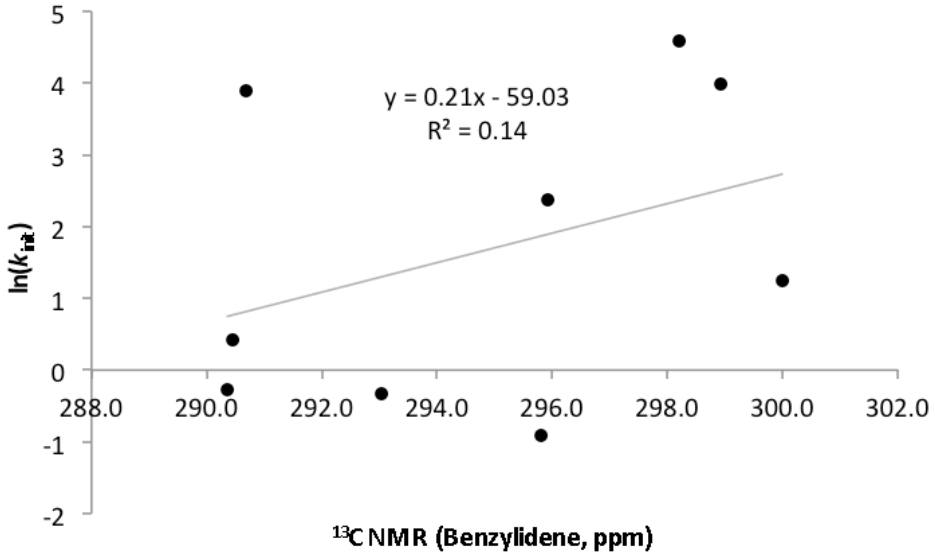


Chart S34: ln(k_{init}) versus Ru–O bond strengths, ΔG_r(**A**→**B**) (Method 1, B3YLP) *with catalyst **7** omitted* (see Chart 13 in the Main Text for comparison).

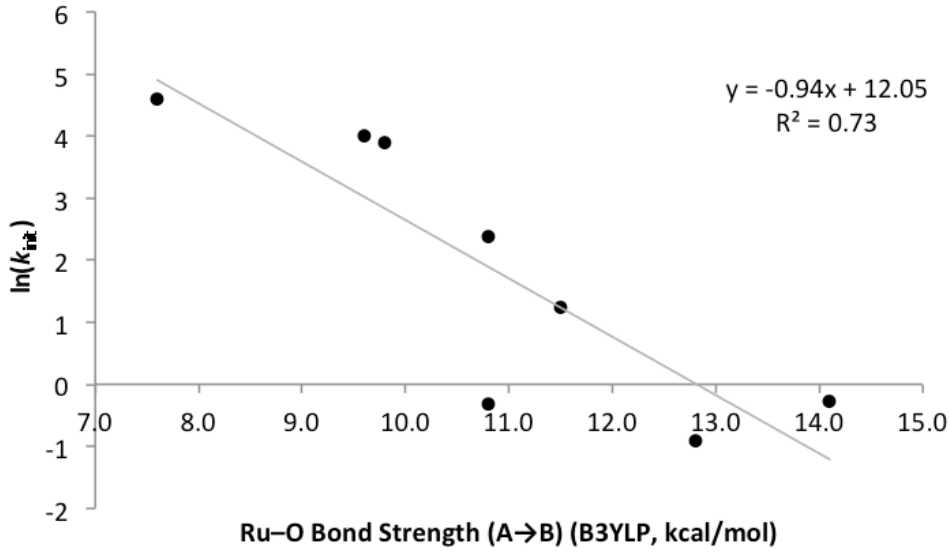
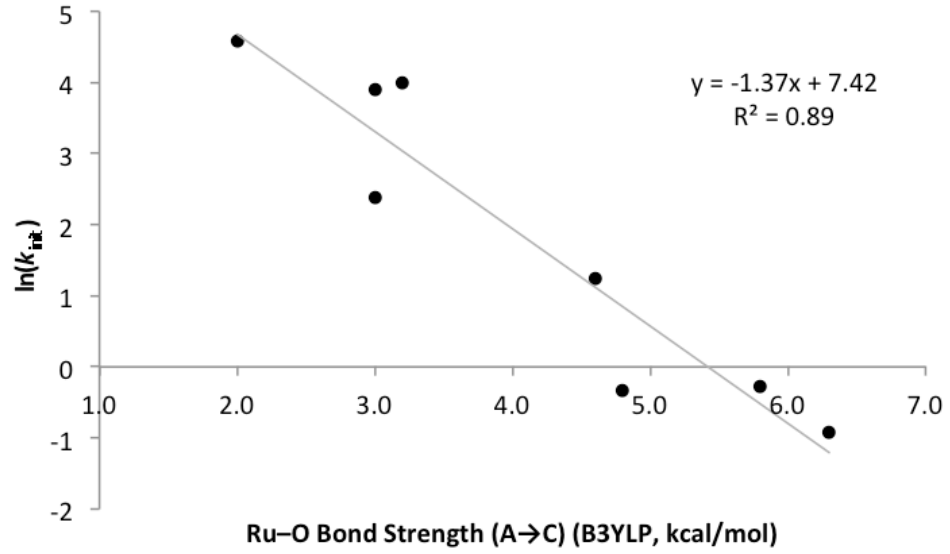


Chart S35: ln(k_{init}) versus Ru–O bond strengths, ΔG_r(**A**→**C**) (Method 2, B3YLP) *with catalyst **7** omitted* (see Chart 14 in the Main Text for comparison).



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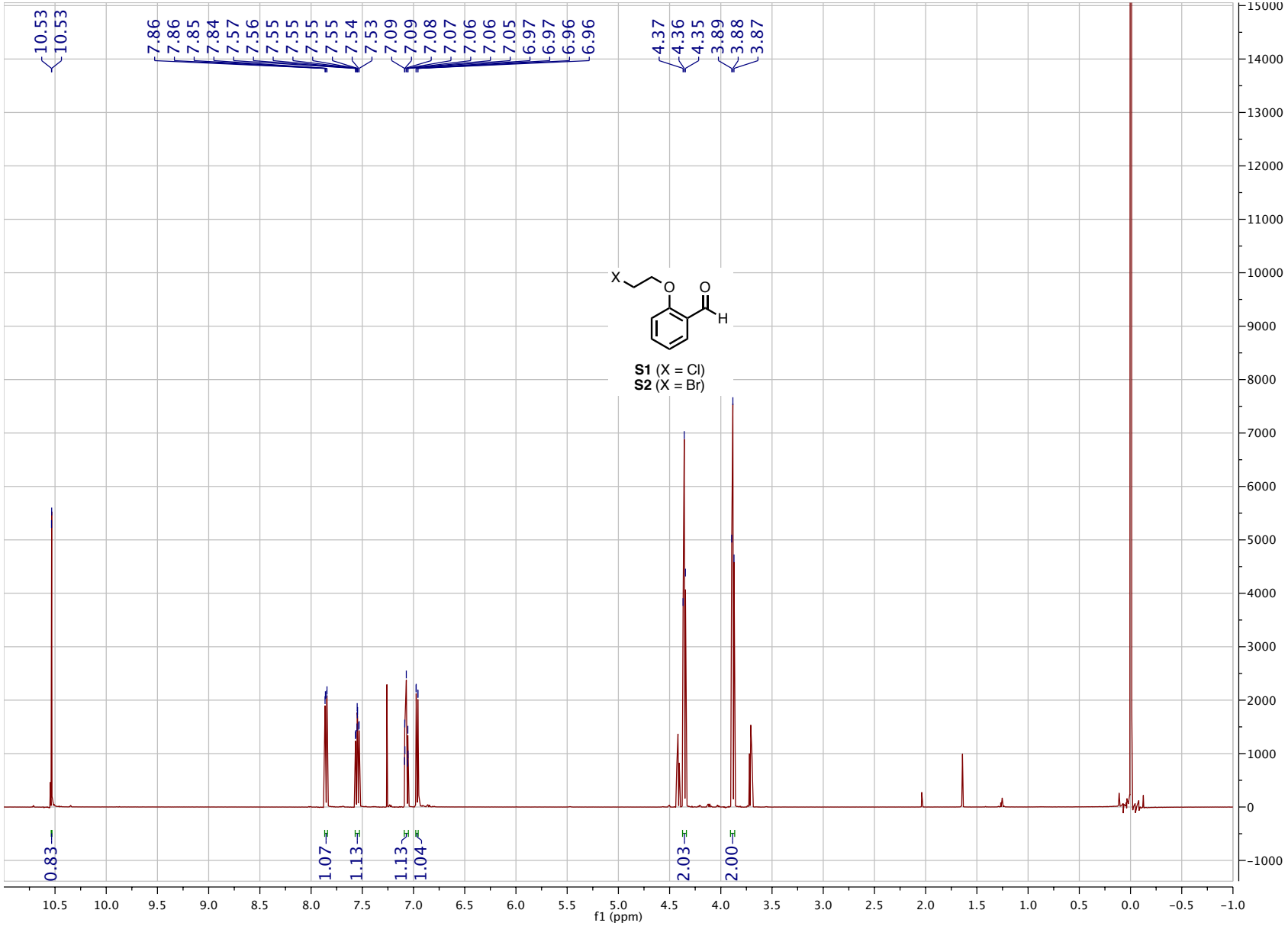
NMR SPECTRA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7.09
7.08
7.07
7.06
7.06
7.05
6.97
6.97
6.96
6.96
4.37
4.36
4.35
3.89
3.88
3.87
X
O
O
H
S1 (X = Cl)
S2 (X = Br)
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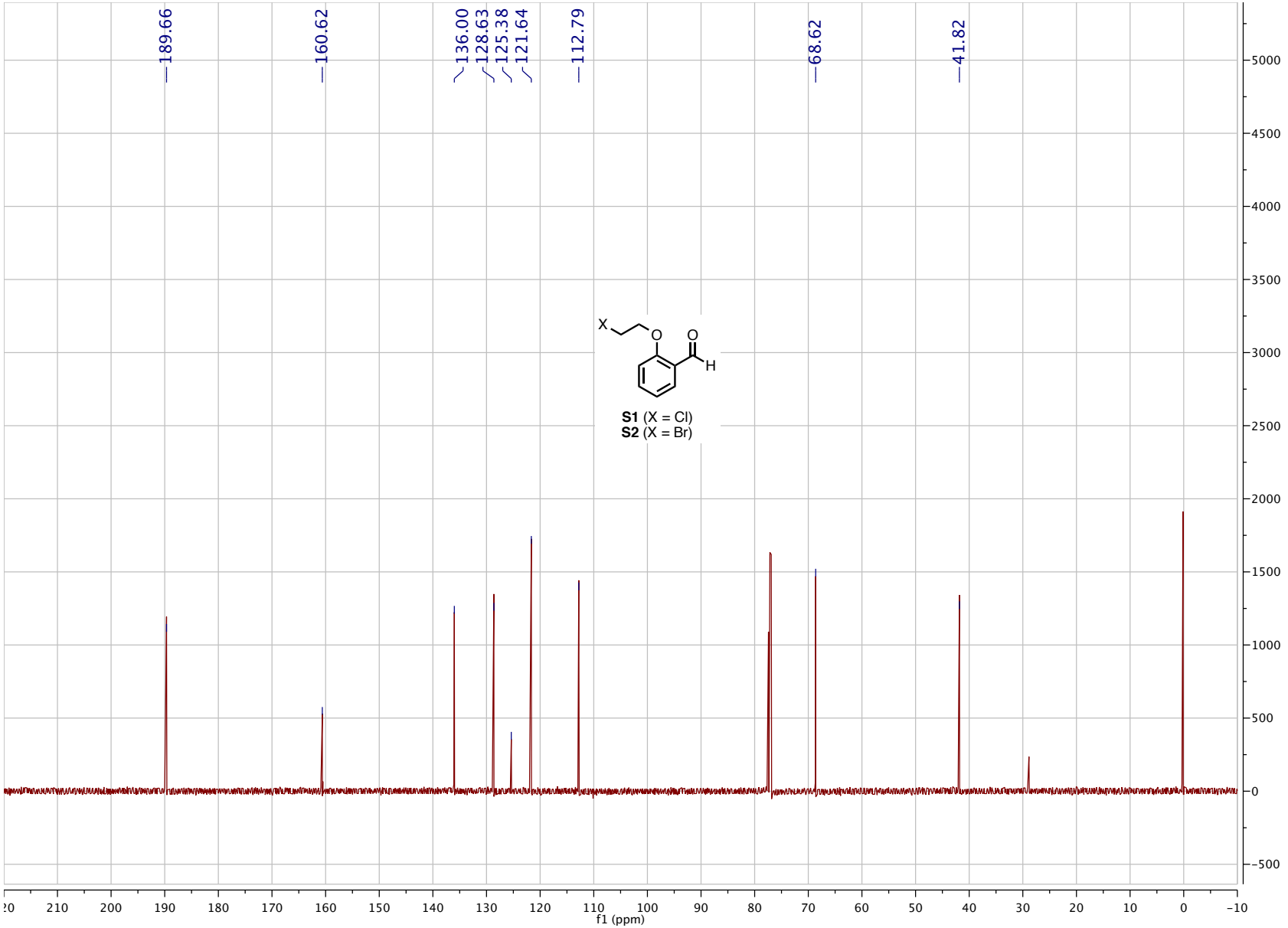
1.07
1.13
1.13
1.04
2.03
2.00
f1 (ppm)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O
H
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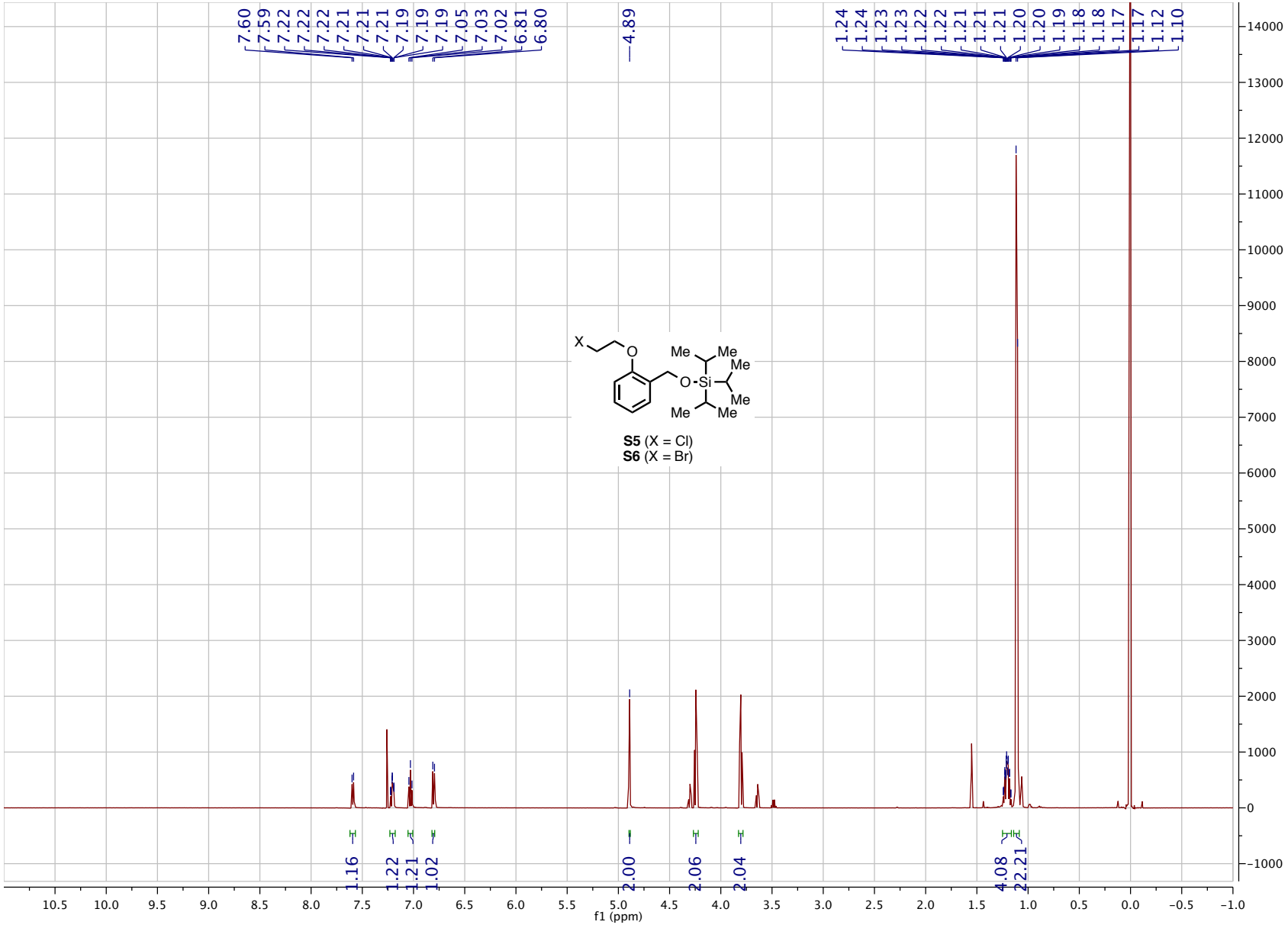
S2 (X = Br)
f1 (ppm)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6.81
6.80
4.89
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1.24
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1.23
1.22
1.22
1.21
1.21
1.21
1.20
1.20
1.19
1.18
1.18
1.17
1.17
1.12
1.10
X
O
Me
Me
Me
O
Si
Me
Me
Me
S5 (X = Cl)
S6 (X = Br)
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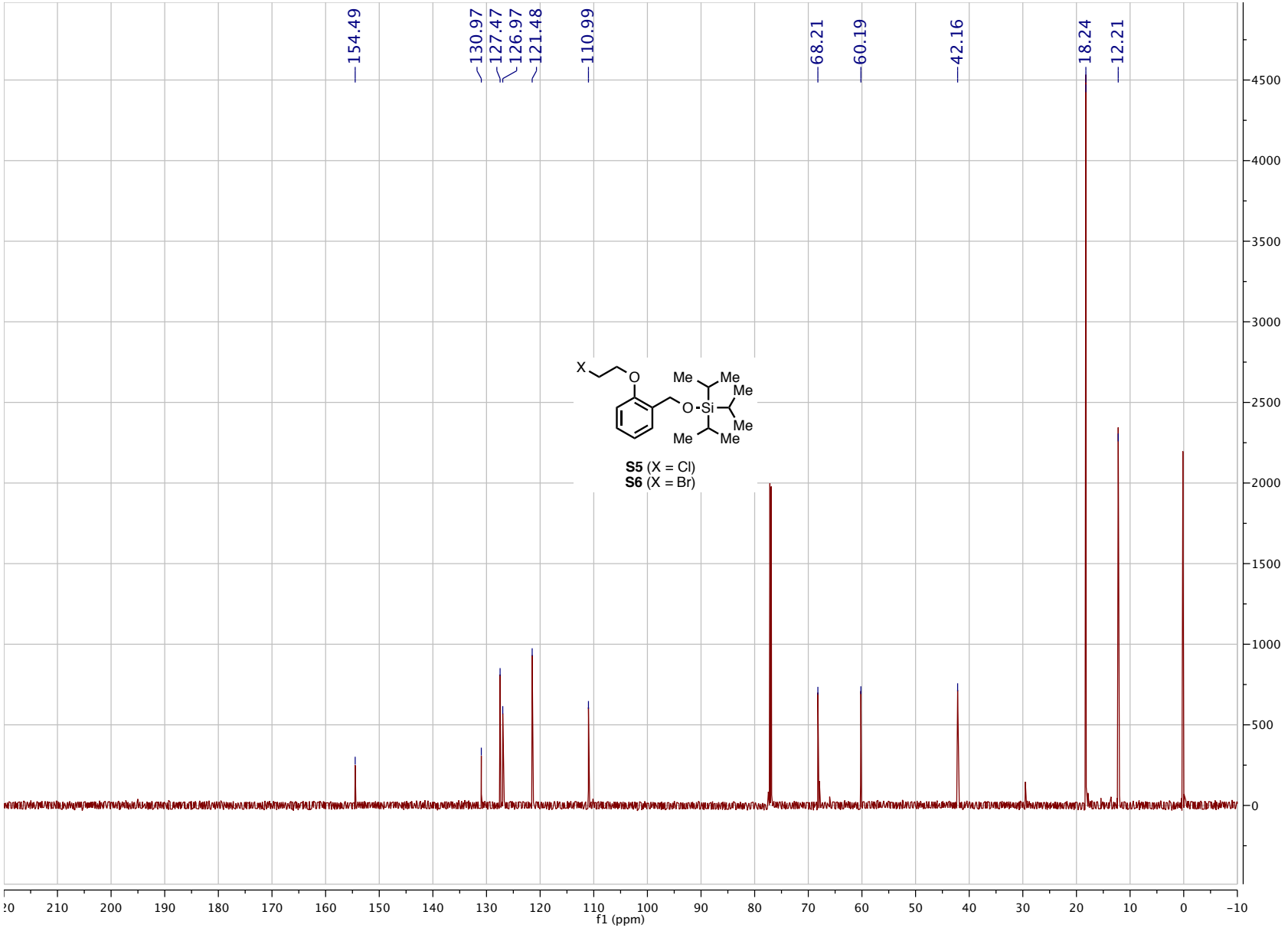
1.21
1.02
2.00
2.06
2.04
4.08
22.21
f1 (ppm)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60.19
42.16
18.24
12.21
X
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Me
Me
O
Si
Me
Me
Me
S5 (X = Cl)
S6 (X = Br)
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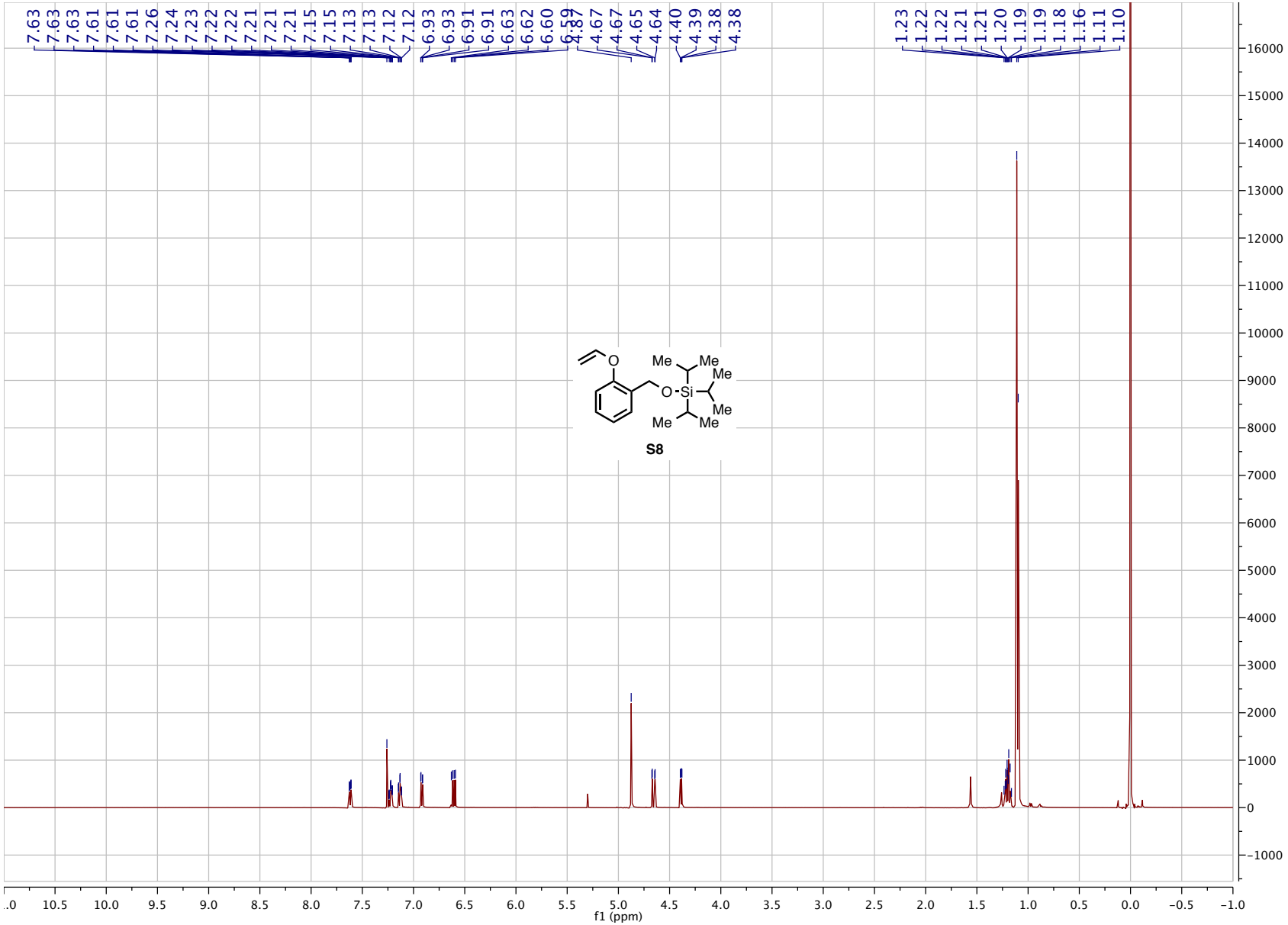
3500
3000
2500
2000
1500
1000
500
0
f1 (ppm)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4.64
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4.39
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4.38
1.23
1.22
1.22
1.21
1.21
1.20
1.19
1.19
1.18
1.16
1.11
1.10
O
Me
Me
Me
O
Si
Me
Me
Me
S8
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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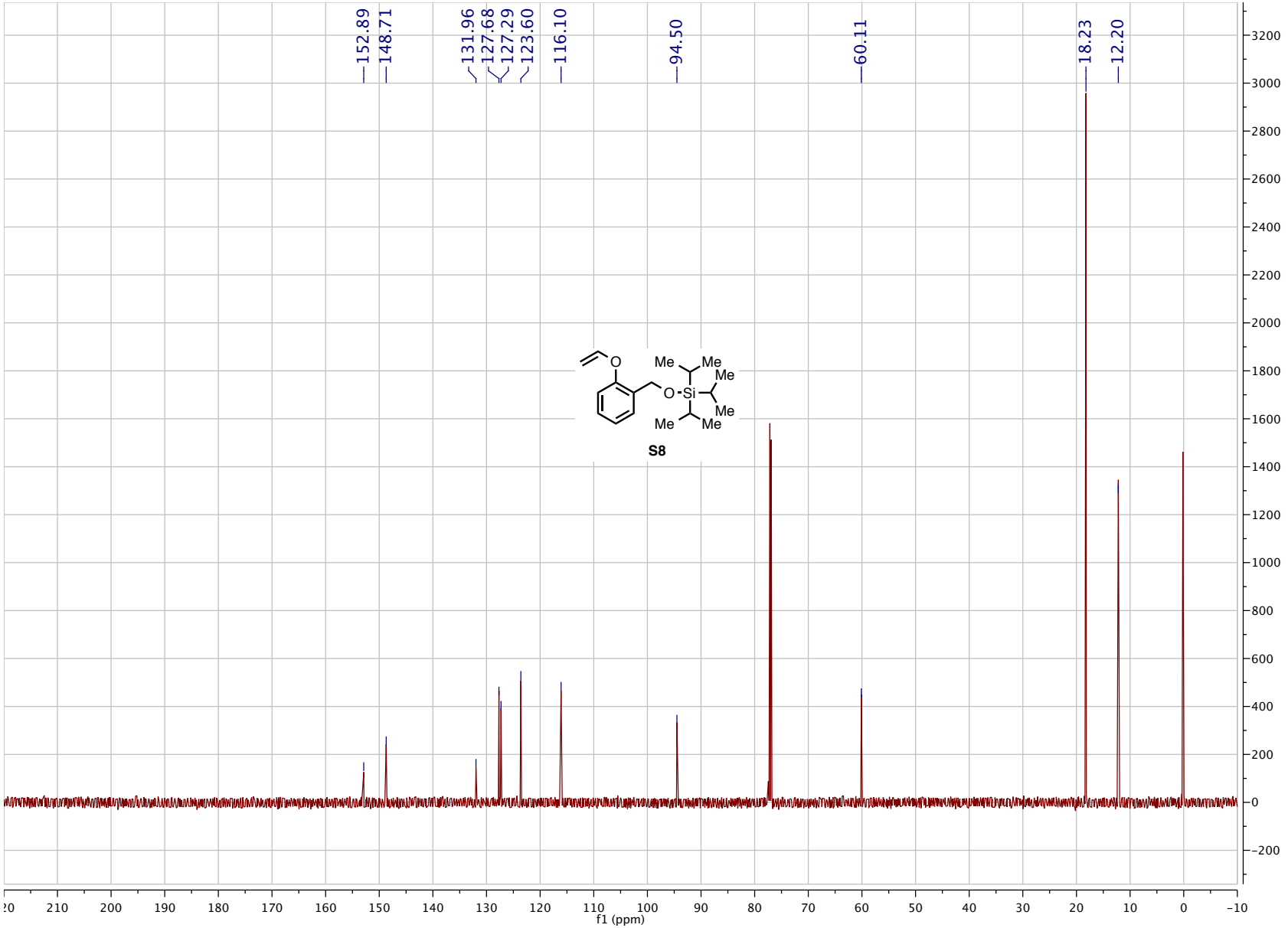
f1 (ppm)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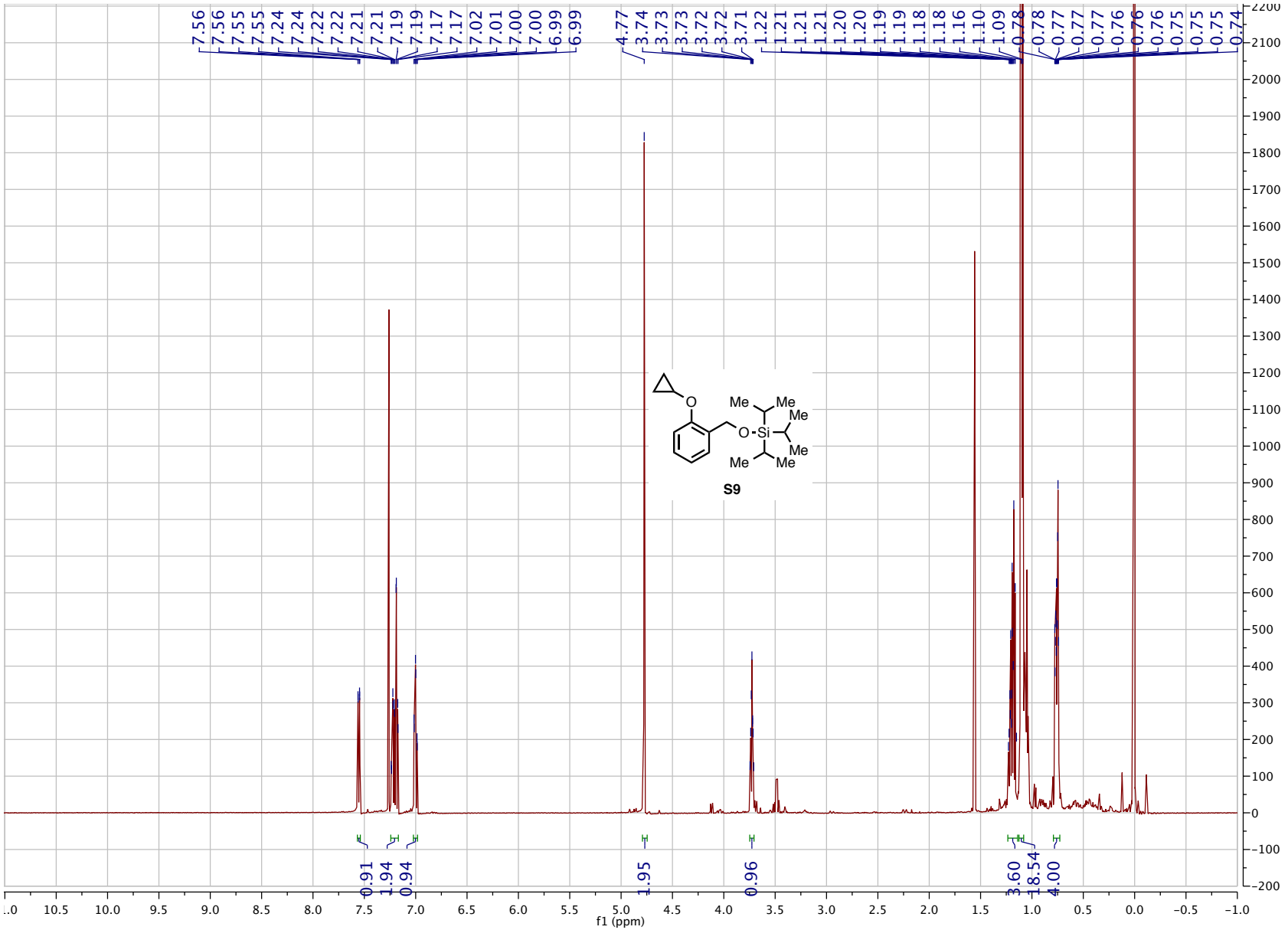
O
Si
Me
Me
Me
S8
f1 (ppm)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4.77 3.74 3.73 3.73 3.72 3.72 3.71 1.22 1.21 1.21 1.21 1.20 1.20 1.19 1.19 1.18 1.18 1.16 1.10 1.09 0.78 0.78 0.77 0.77 0.77 0.76 0.76 0.76 0.75 0.75 0.75 0.74
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Me Me
Me
O Si
Me
Me Me
S9
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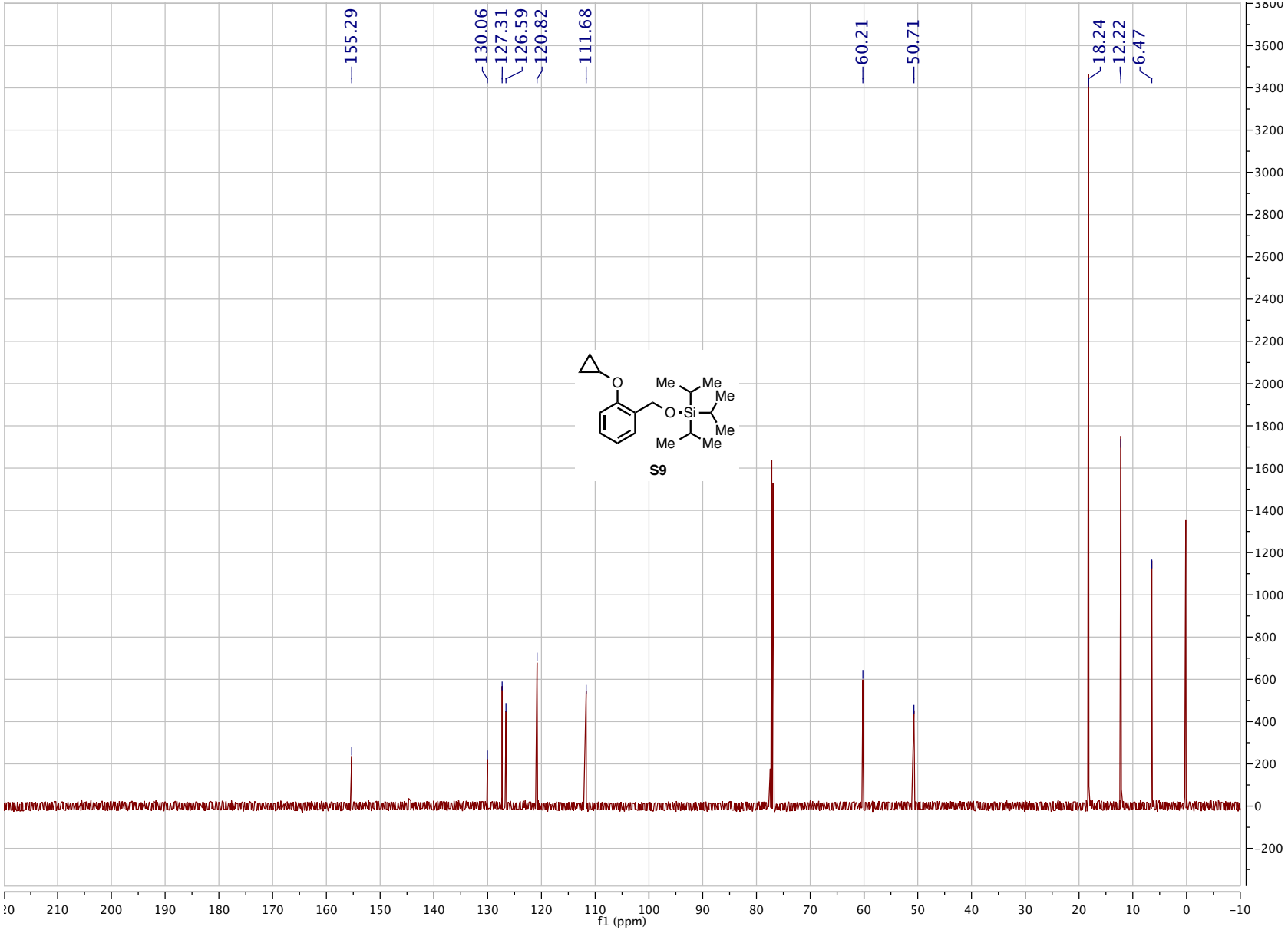
f1 (ppm)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Me
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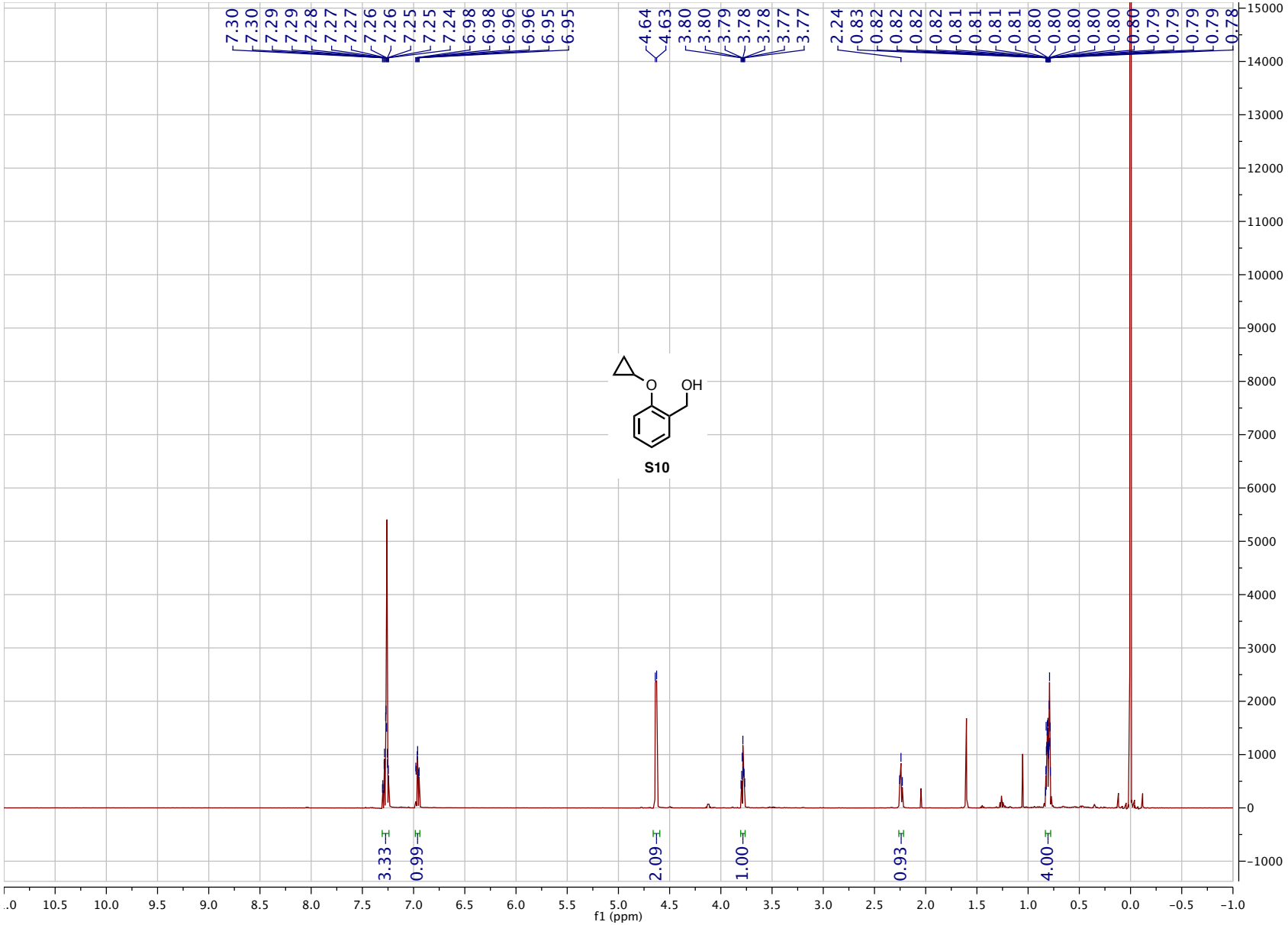
Me
S9
f1 (ppm)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3.80
3.79
3.78
3.78
3.77
3.77
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0.82
0.82
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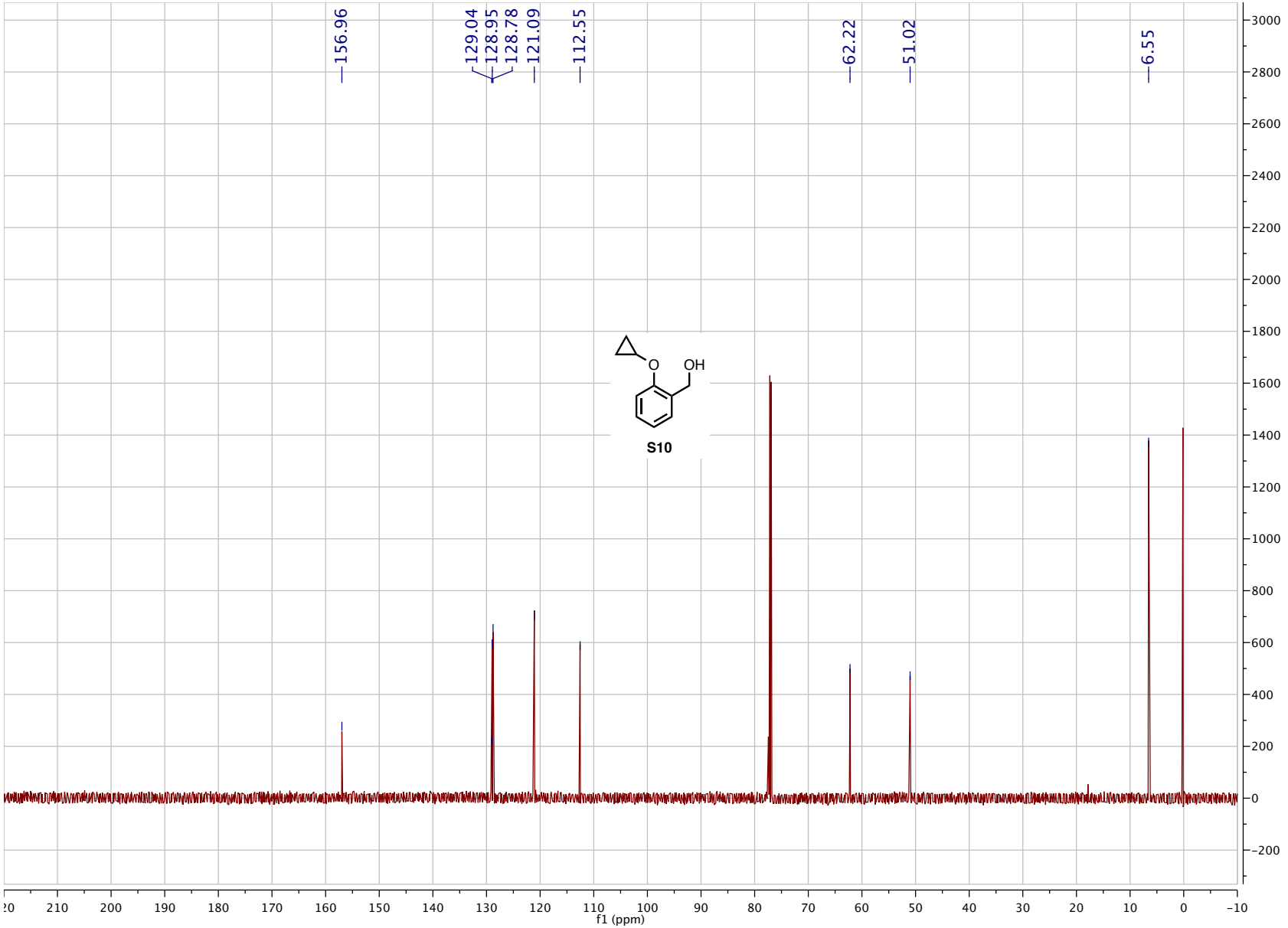
4.00
f1 (ppm)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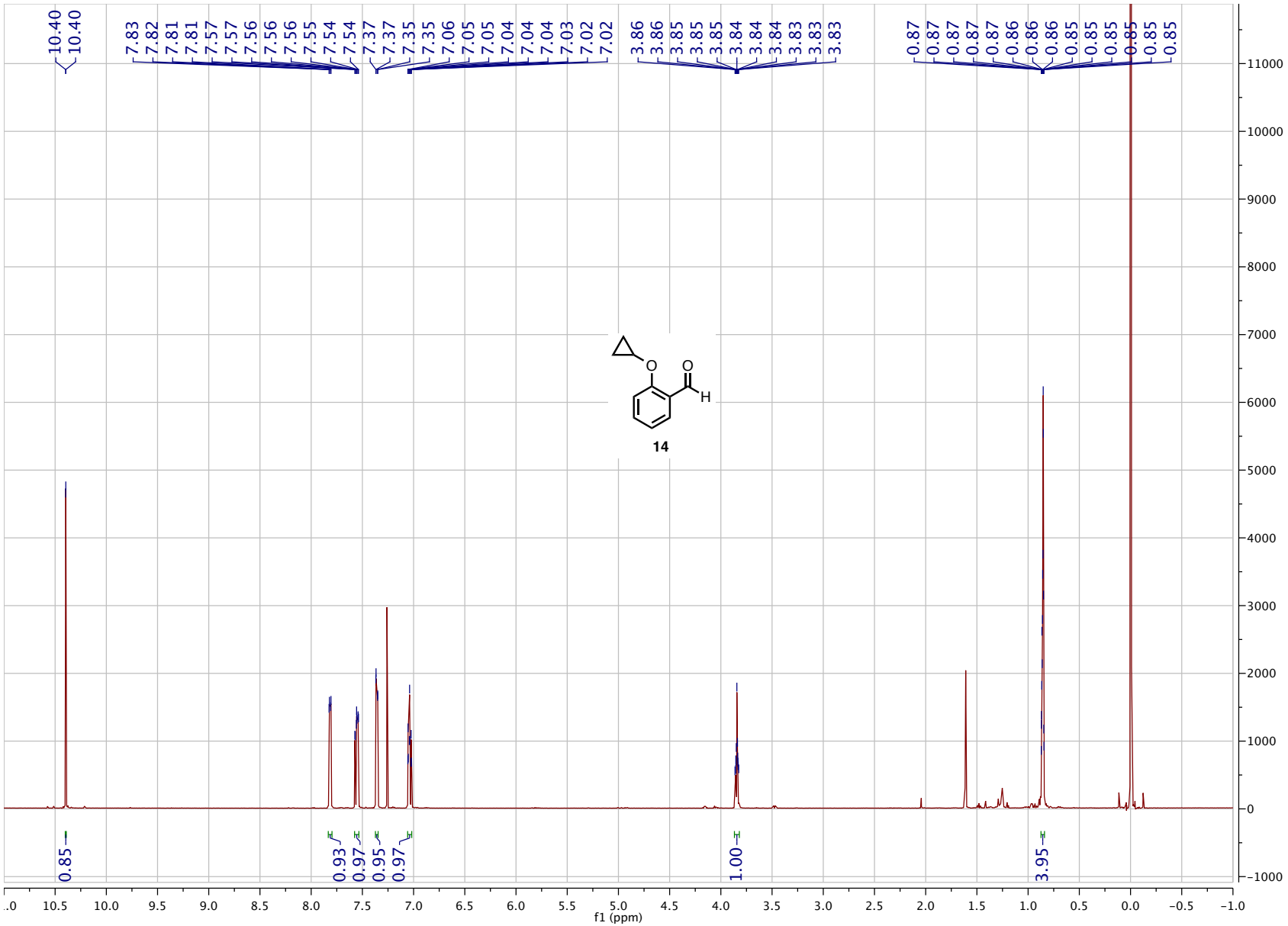
OH
S10
f1 (ppm)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0.85
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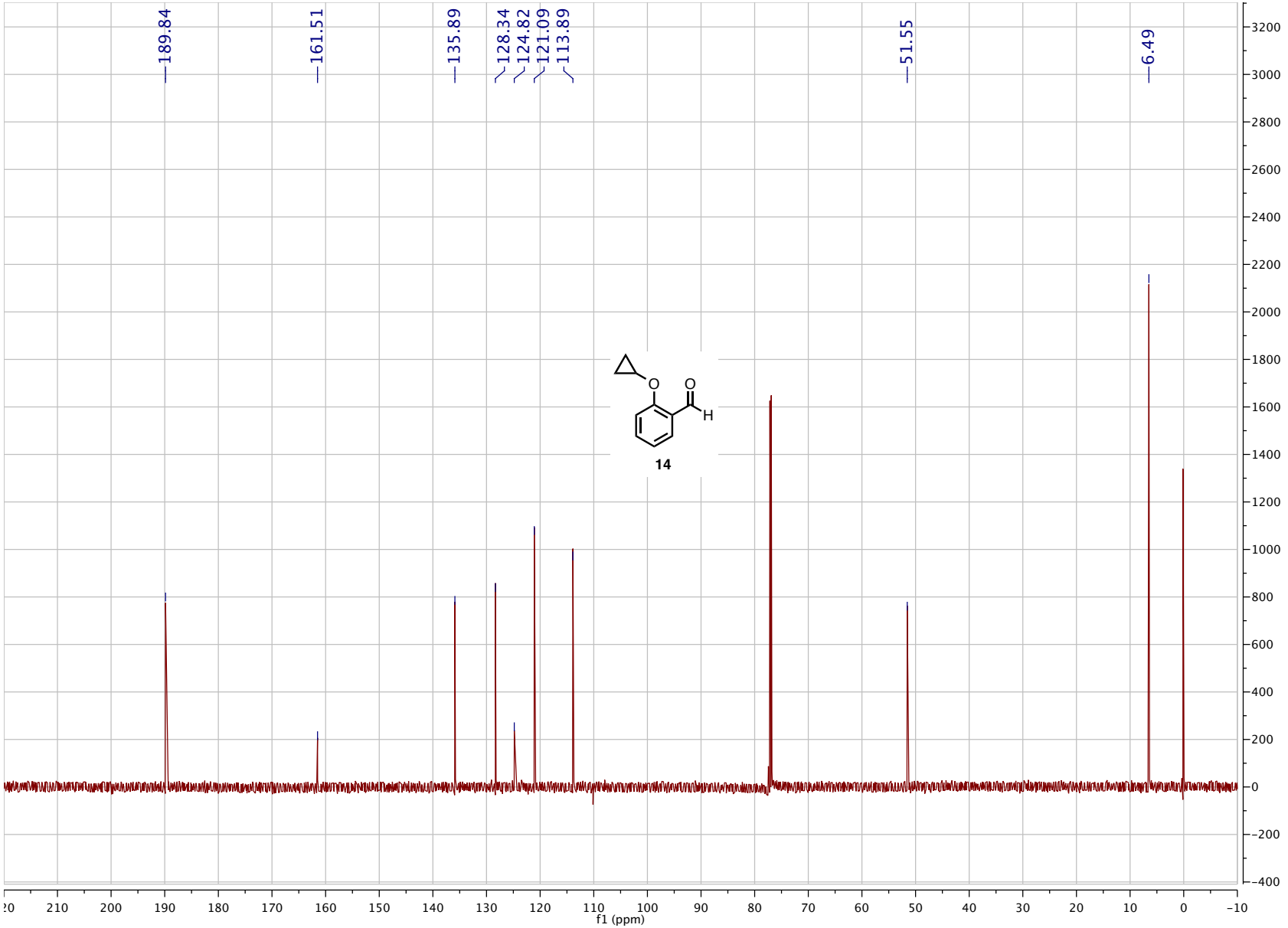
f1 (ppm)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H
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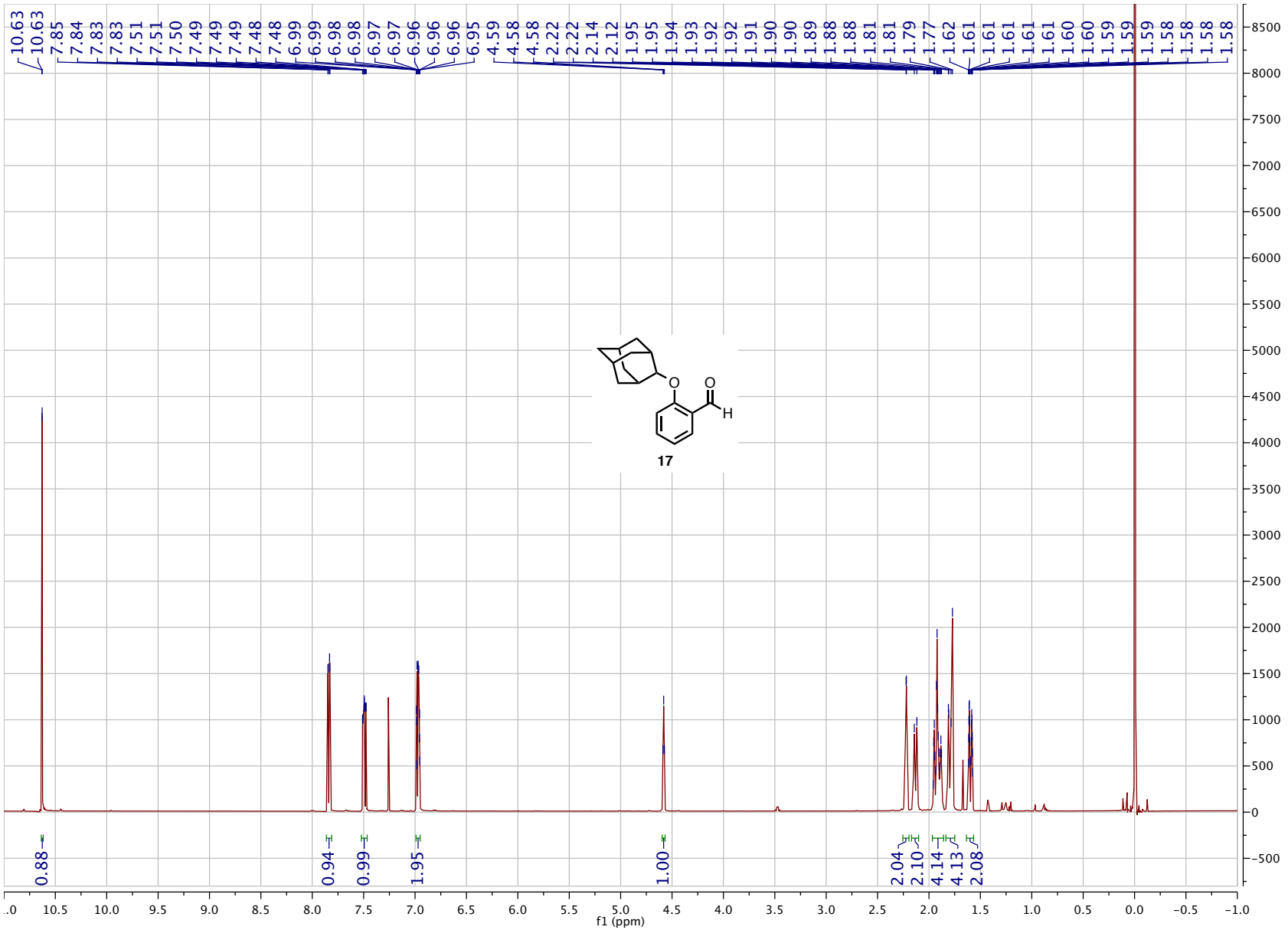
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O
H
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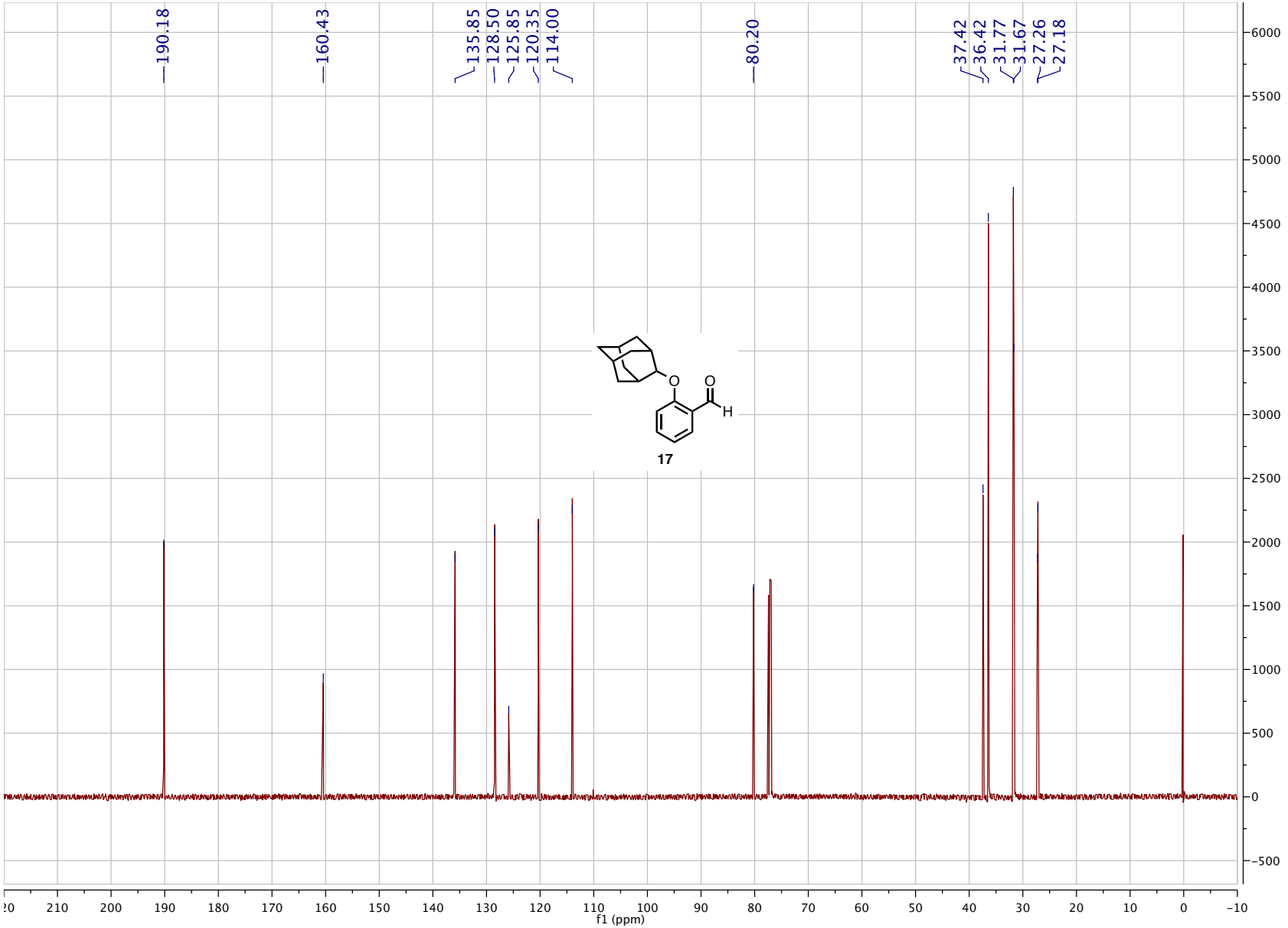
f1 (ppm)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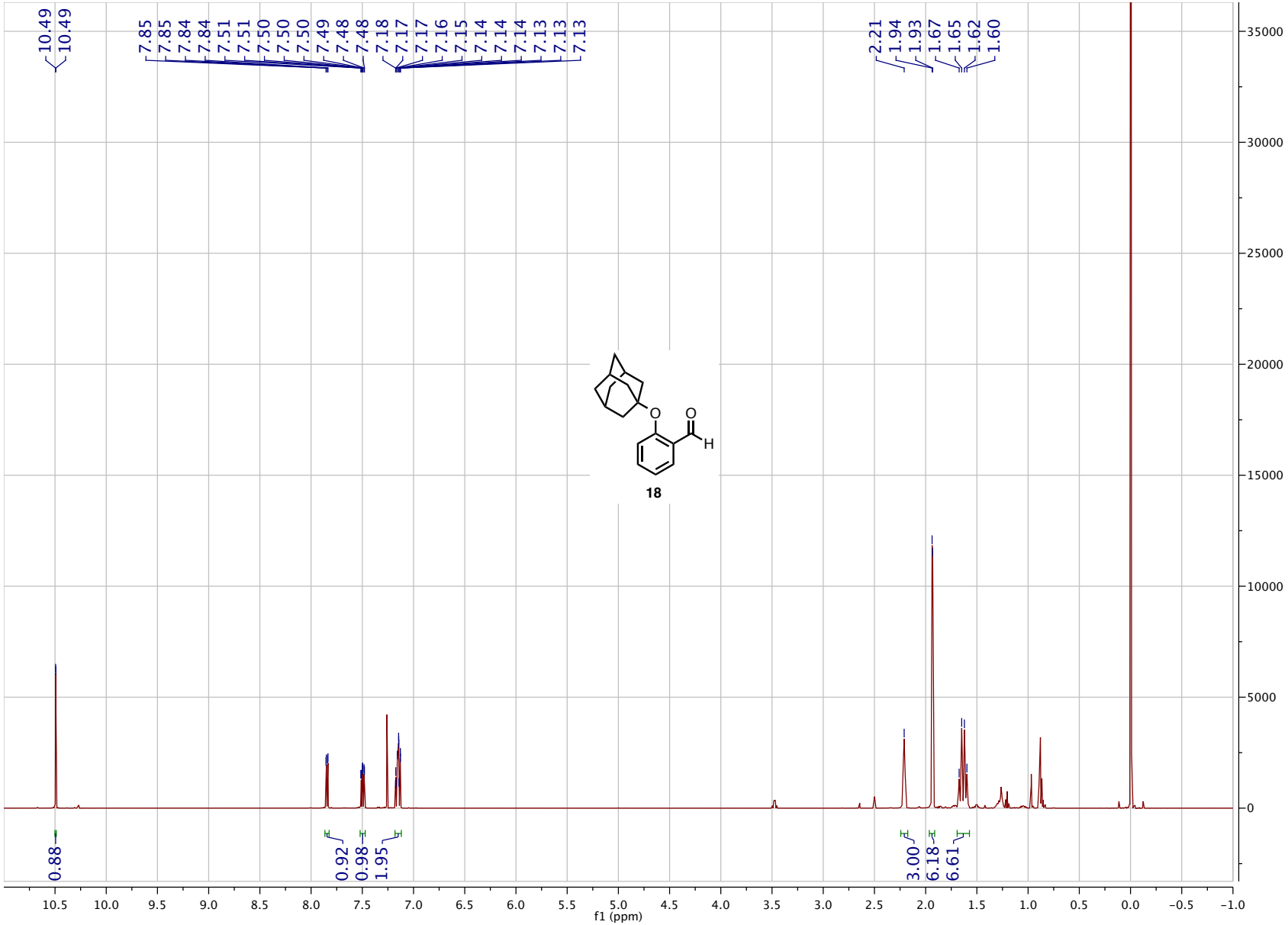
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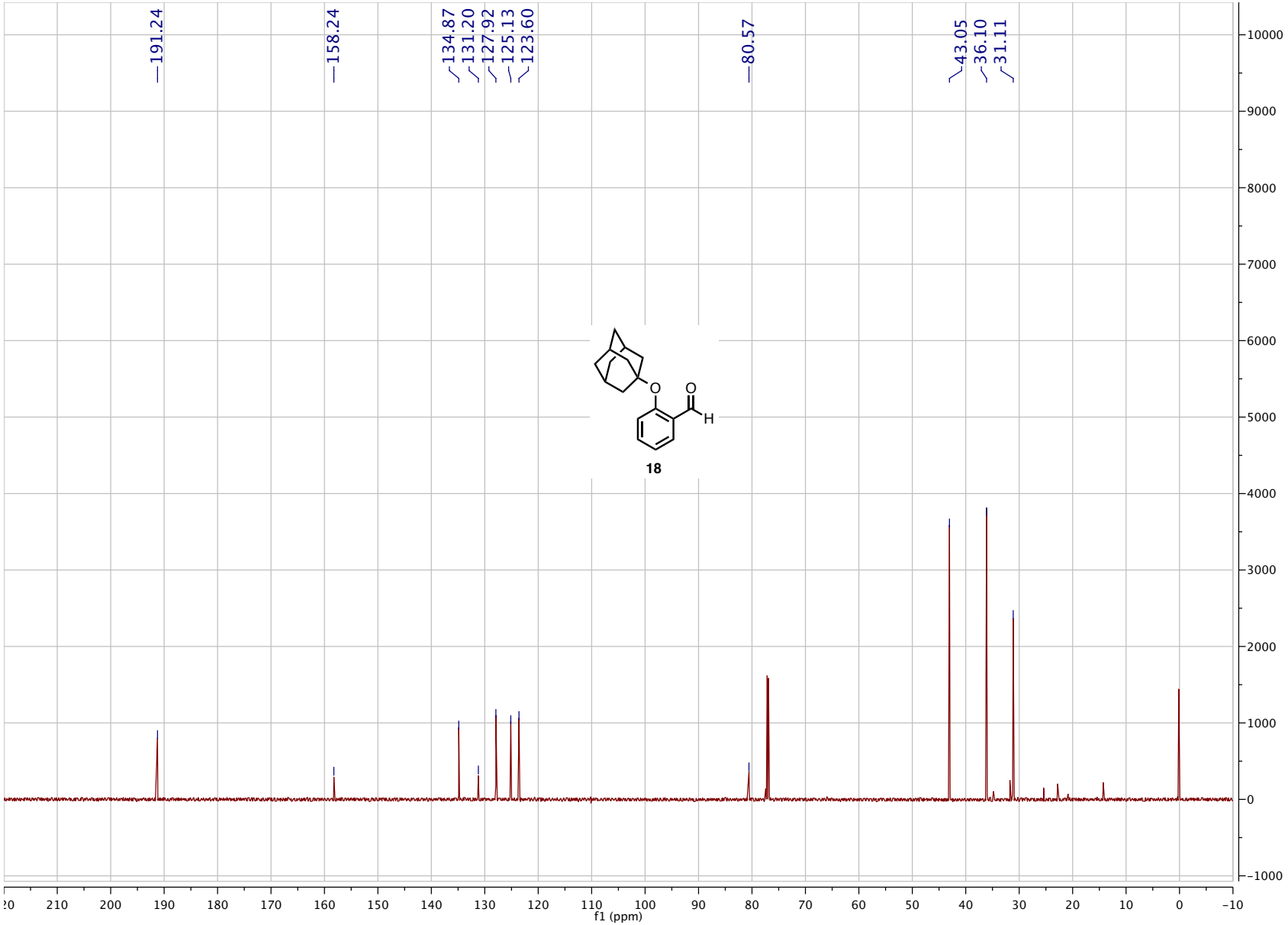
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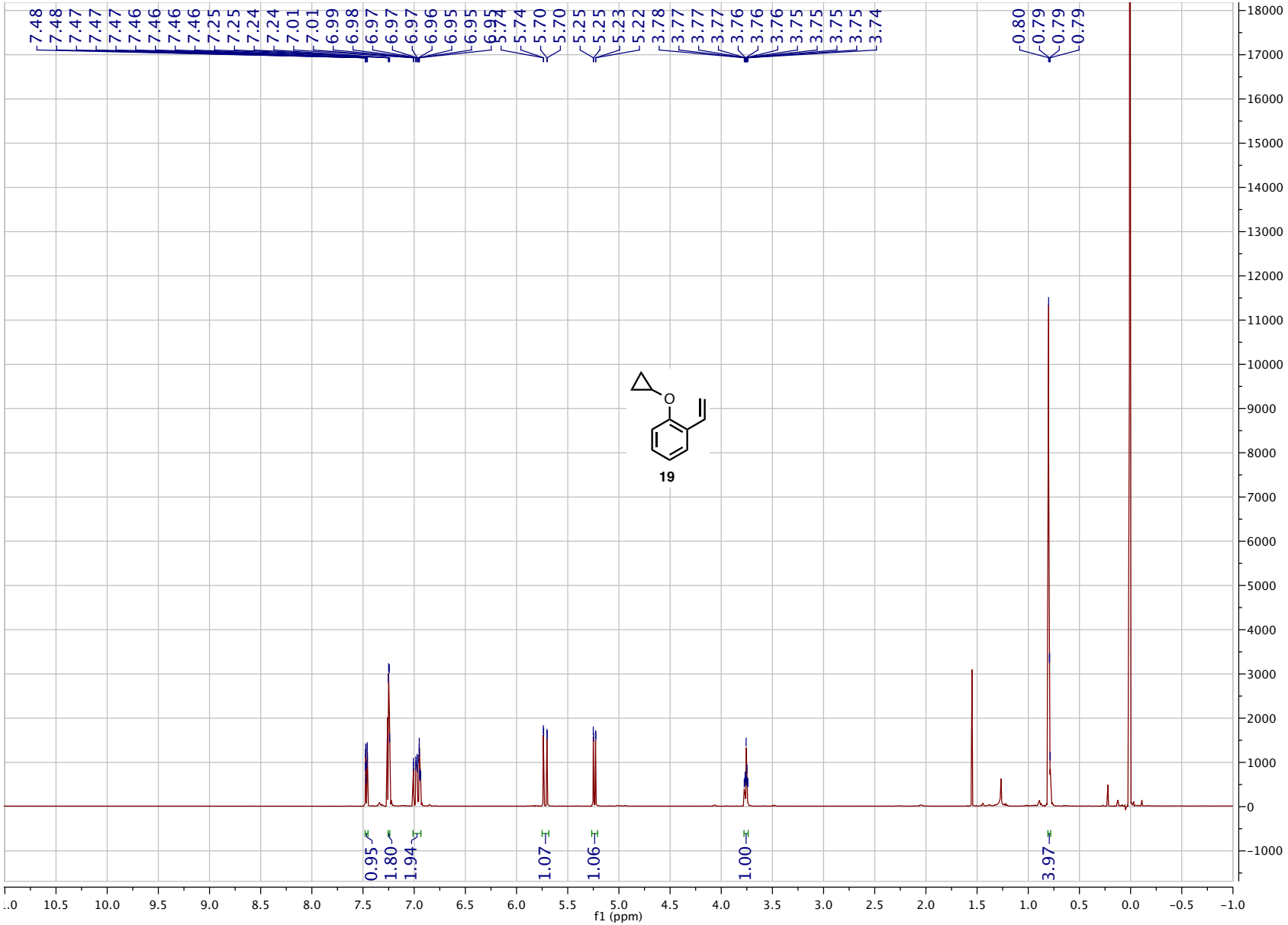
f1 (ppm)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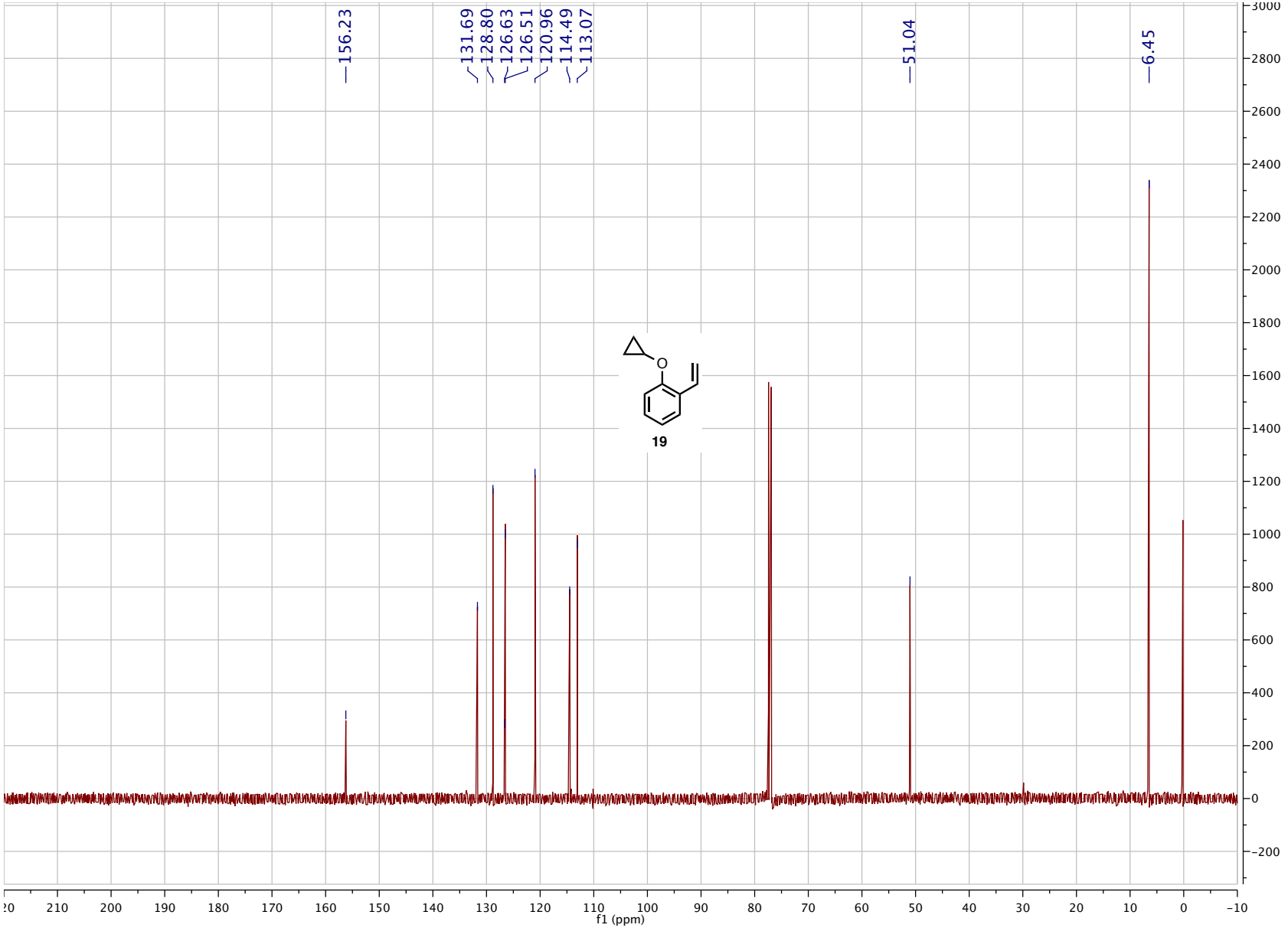
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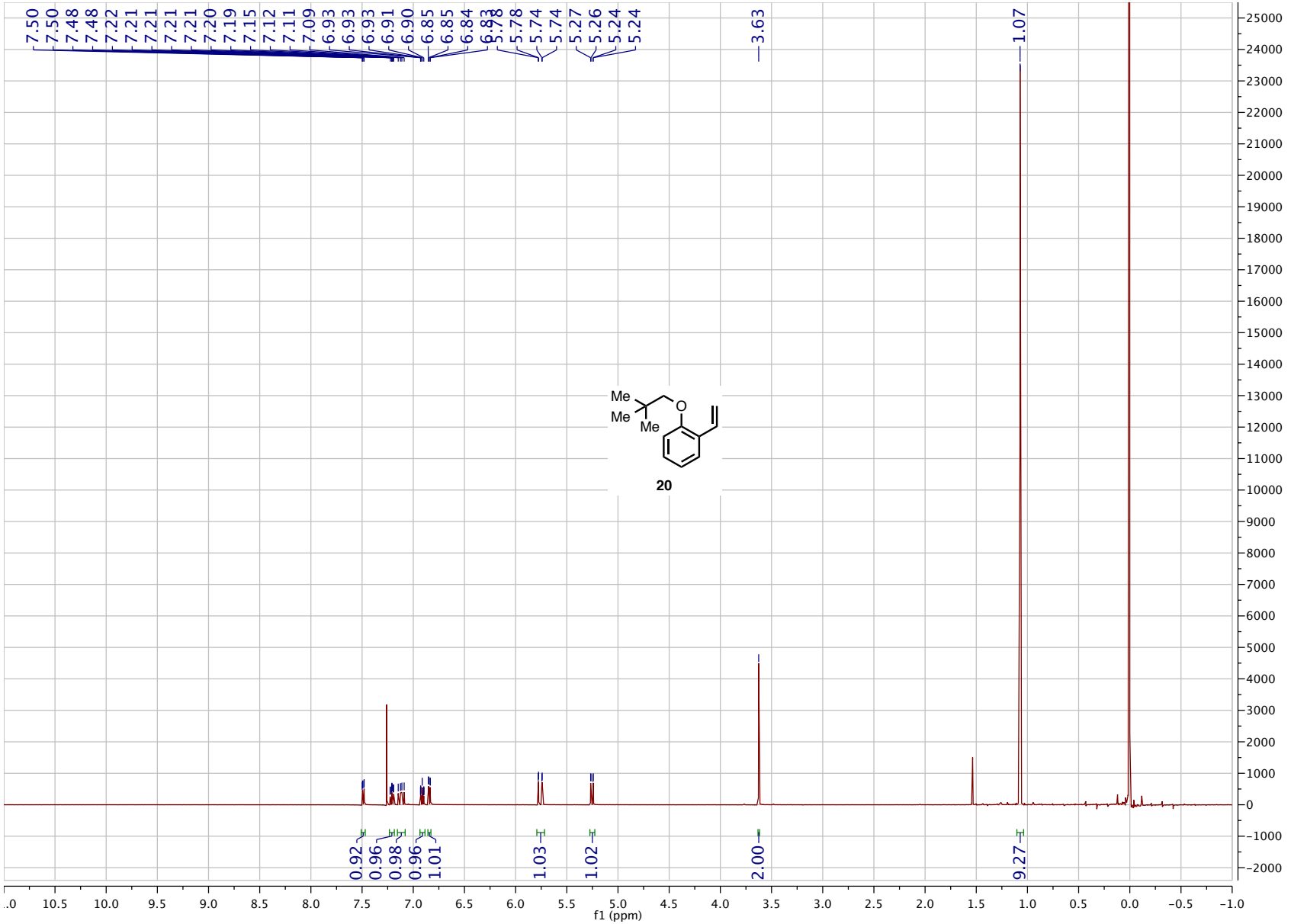
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6.85
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6.84
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5.78
5.74
5.74
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5.26
5.24
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3.63
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Me
Me
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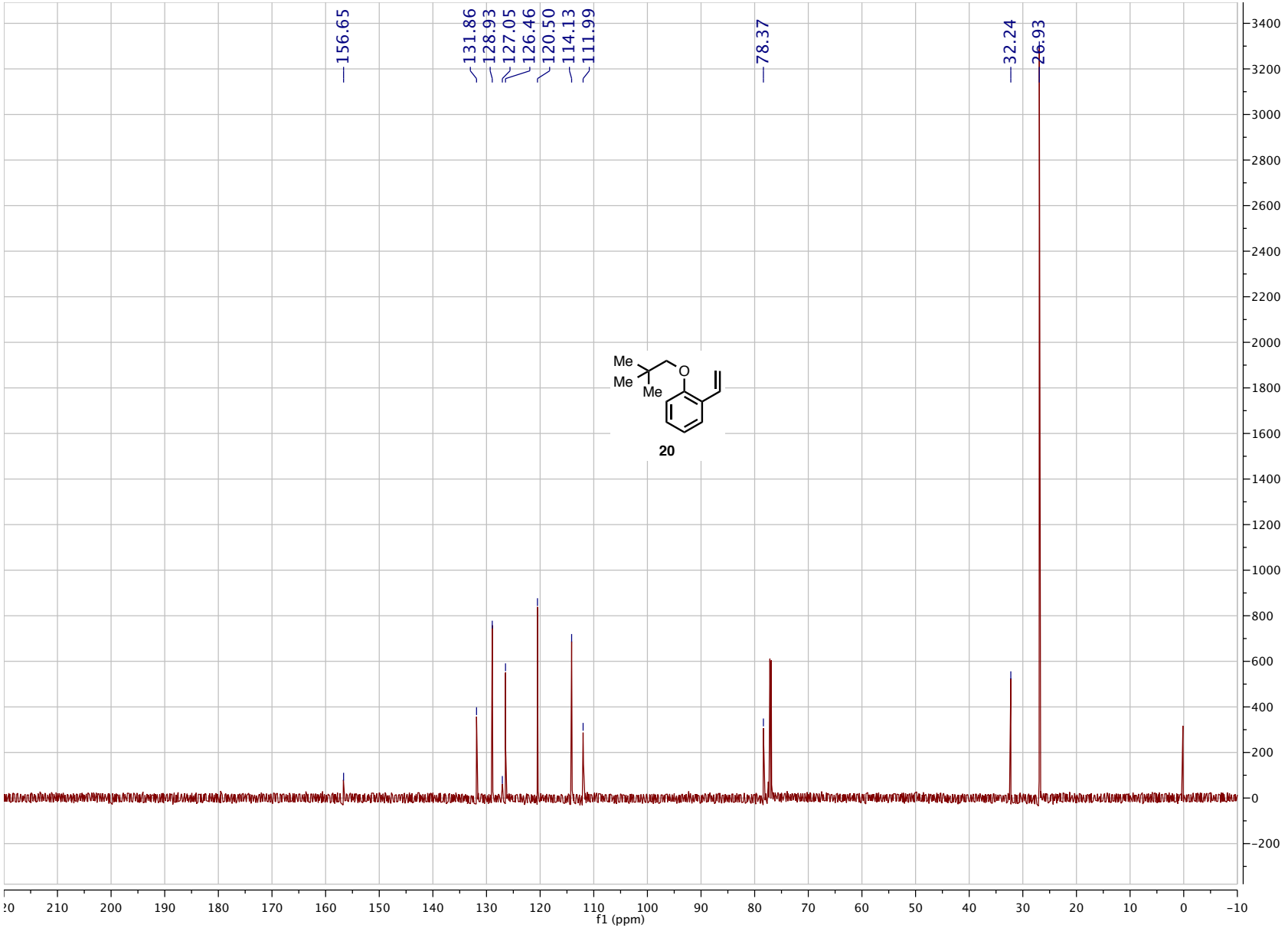
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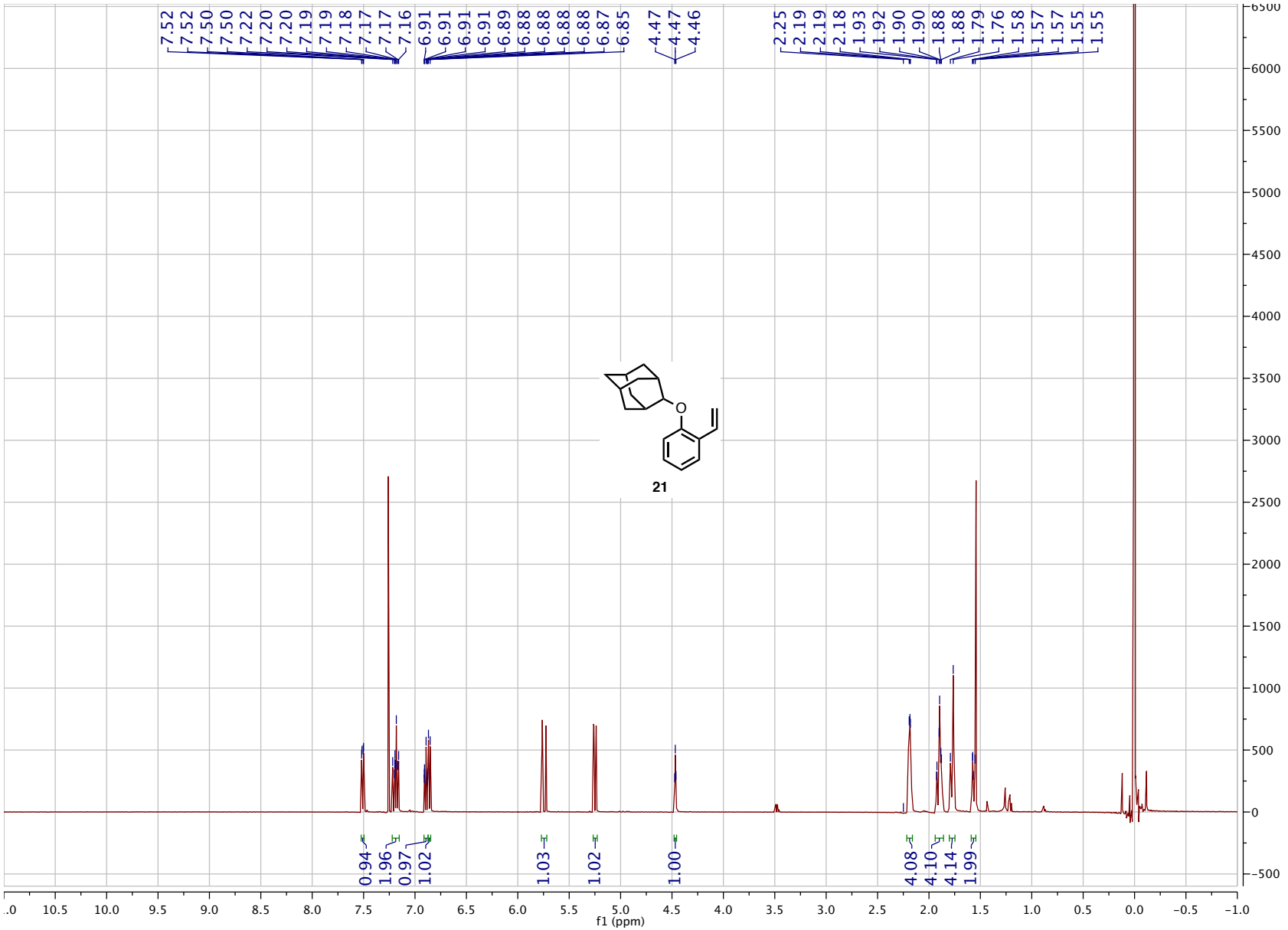
f1 (ppm)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1.90
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1.55
1.55
O
21
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1.00
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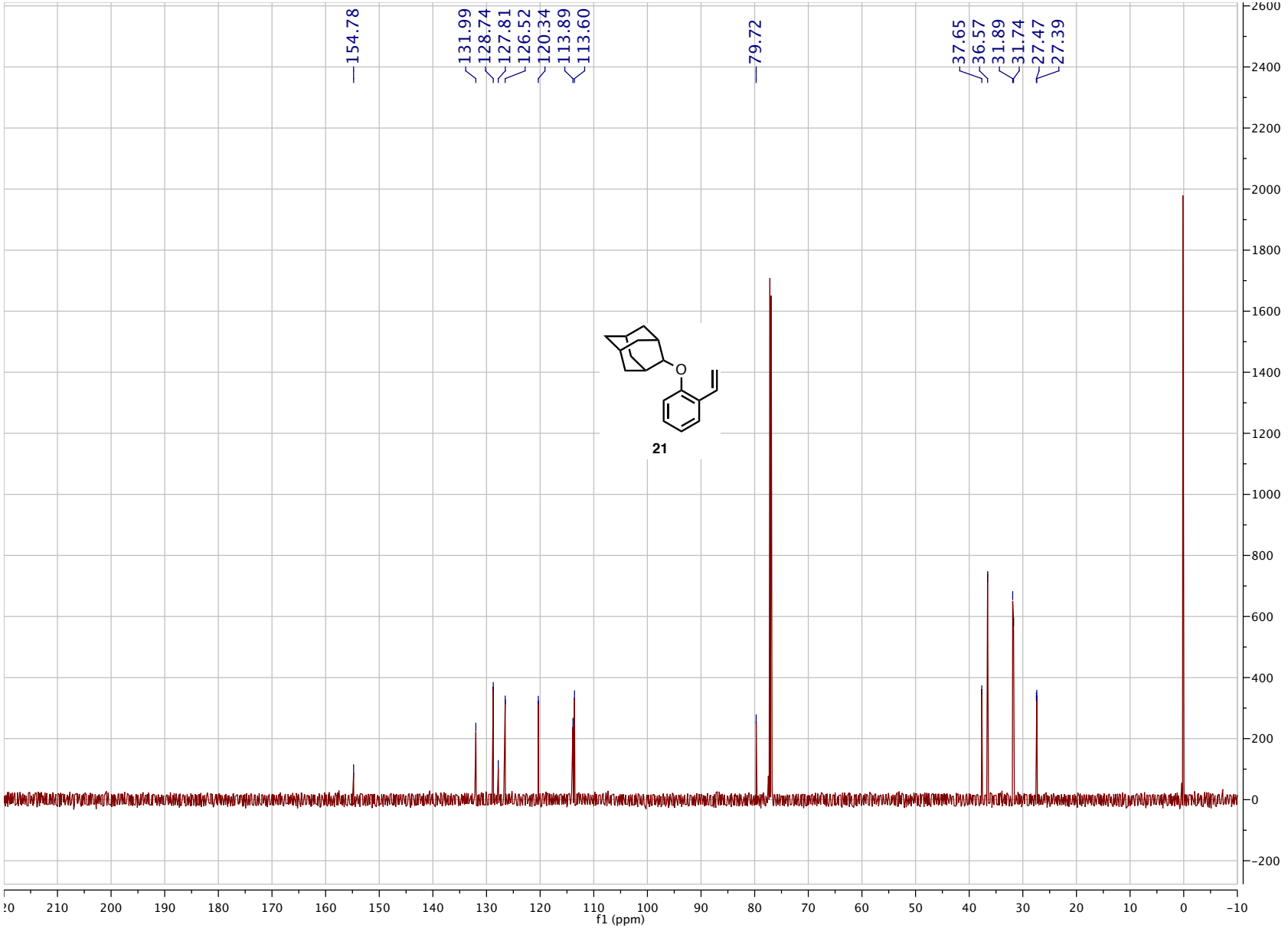
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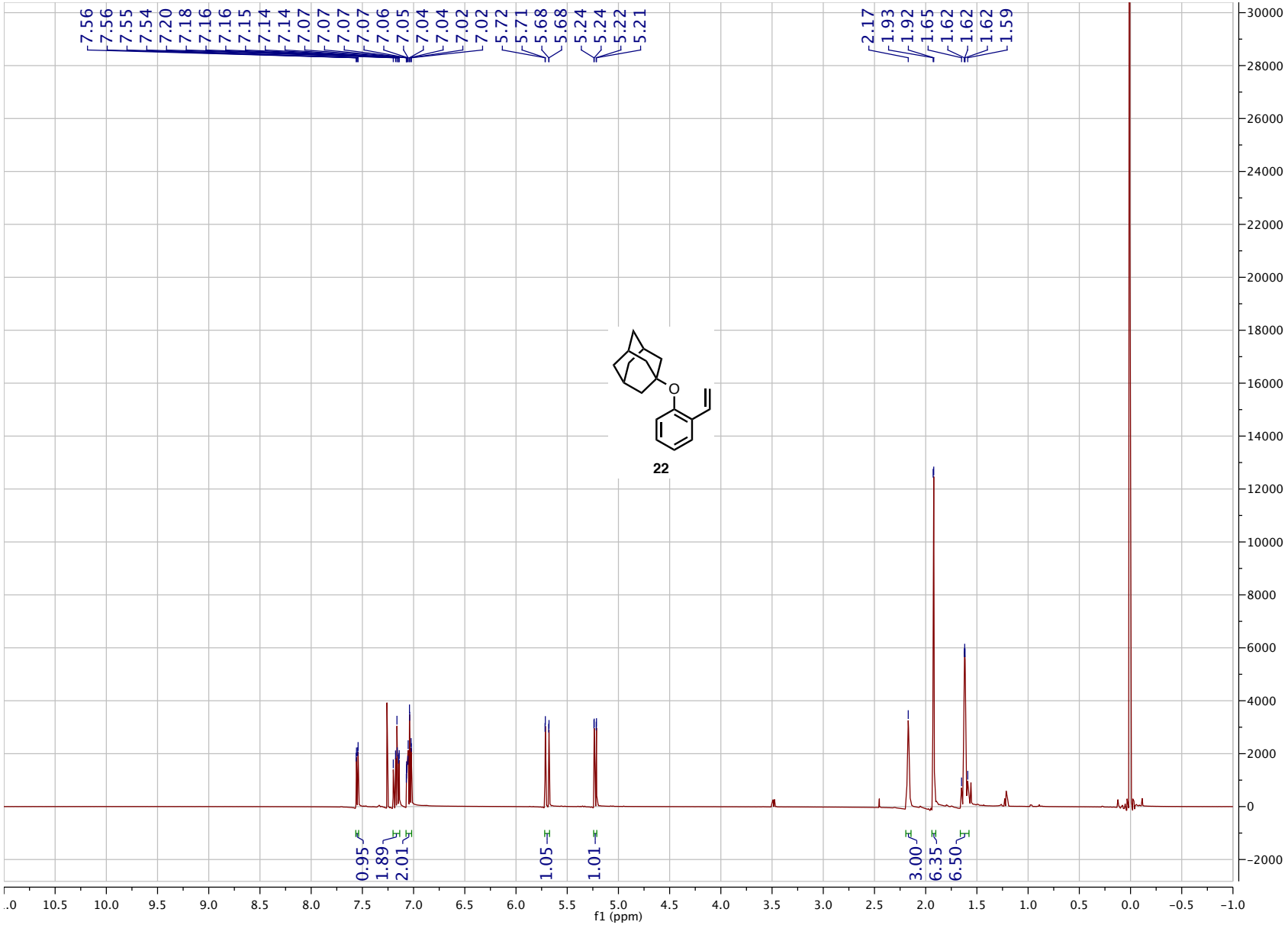
27.47
27.39
O
21
f1 (ppm)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7.14
7.07
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7.07
7.07
7.06
7.05
7.04
7.04
7.02
7.02
5.72
5.71
5.68
5.68
5.24
5.24
5.22
5.21
2.17
1.93
1.92
1.65
1.62
1.62
1.62
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22
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1.89
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1.05
1.01
3.00
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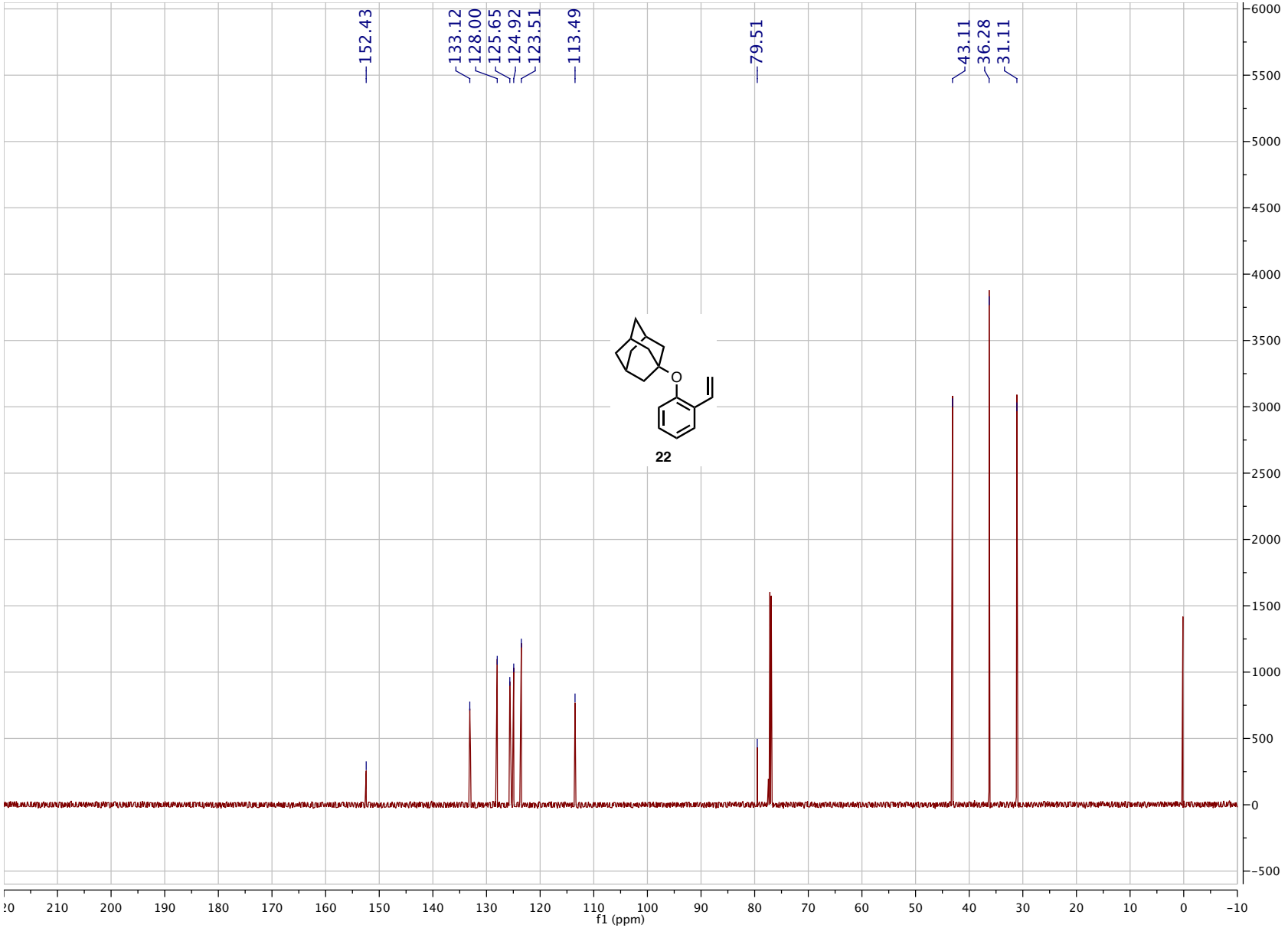
6.50
f1 (ppm)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123.51
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79.51
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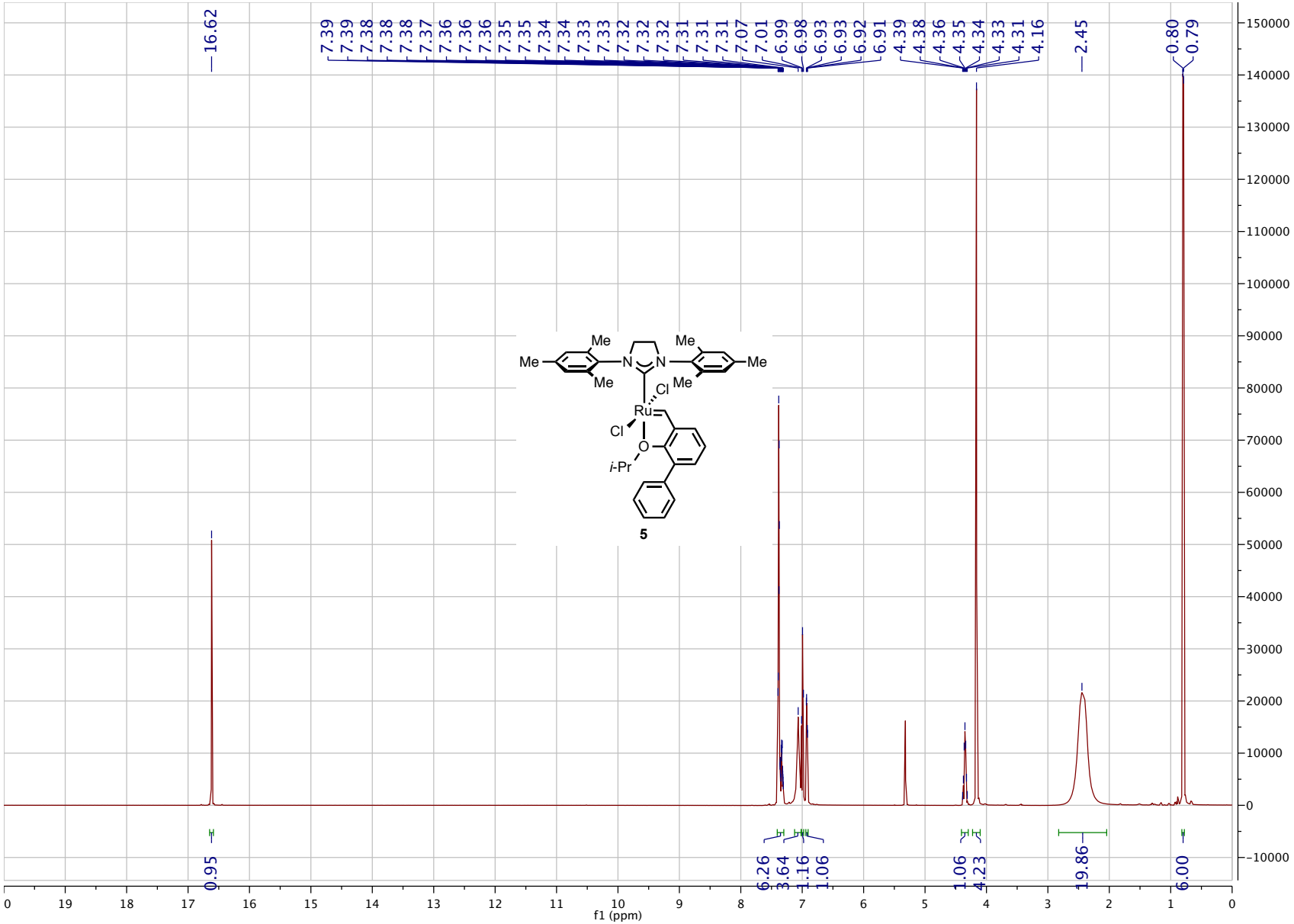
36.28
31.11
O
22
f1 (ppm)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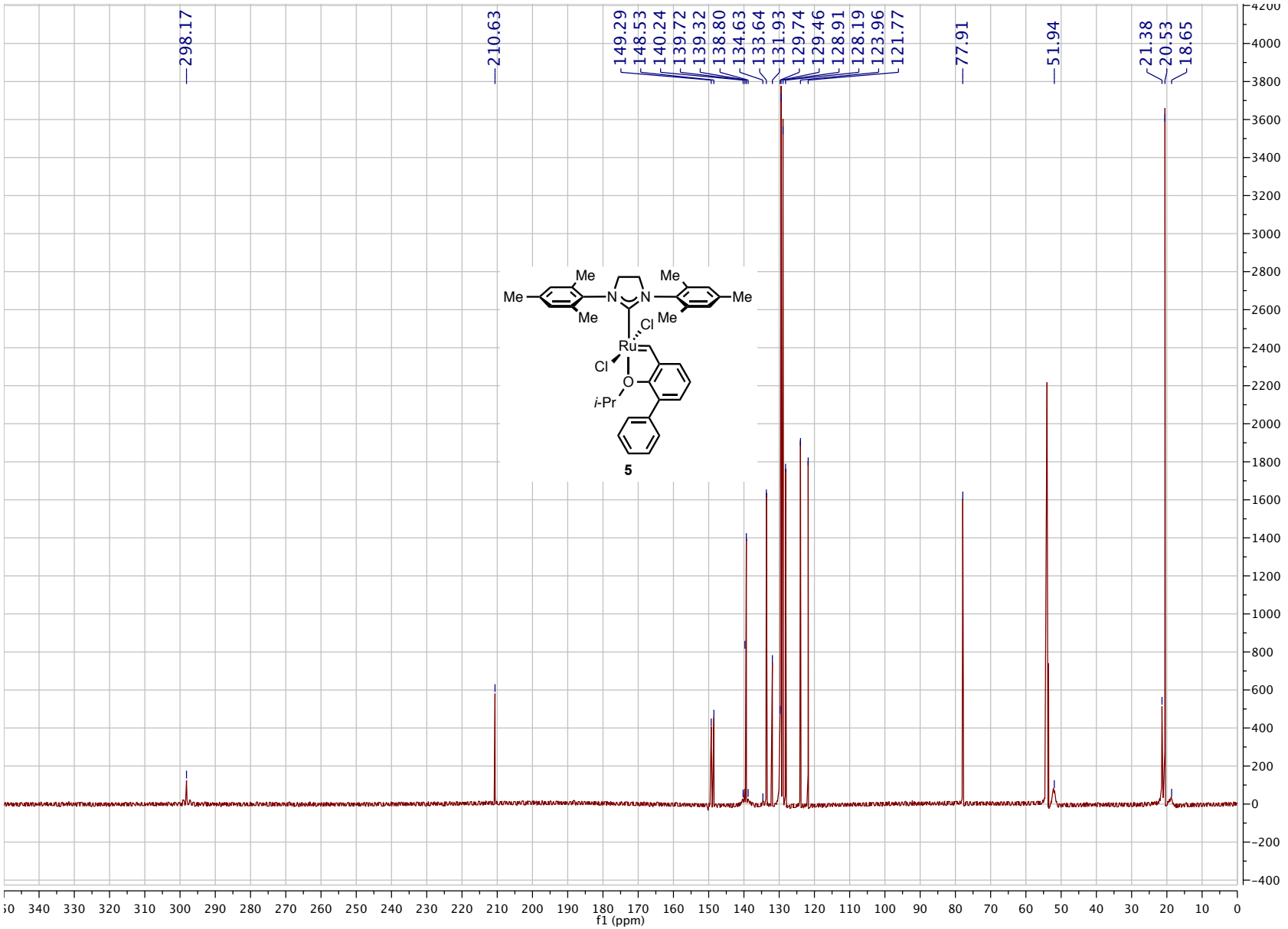
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.07
7.01
6.99
6.98
6.93
6.93
6.92
6.91
4.39
4.38
4.36
4.35
4.34
4.33
4.31
4.16
2.45
0.80
0.79
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
i-Pr
5
0.95
6.26
3.64
1.16
1.06
1.06
4.23
19.86
6.00
f1 (ppm)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149.29
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139.72
139.32
138.80
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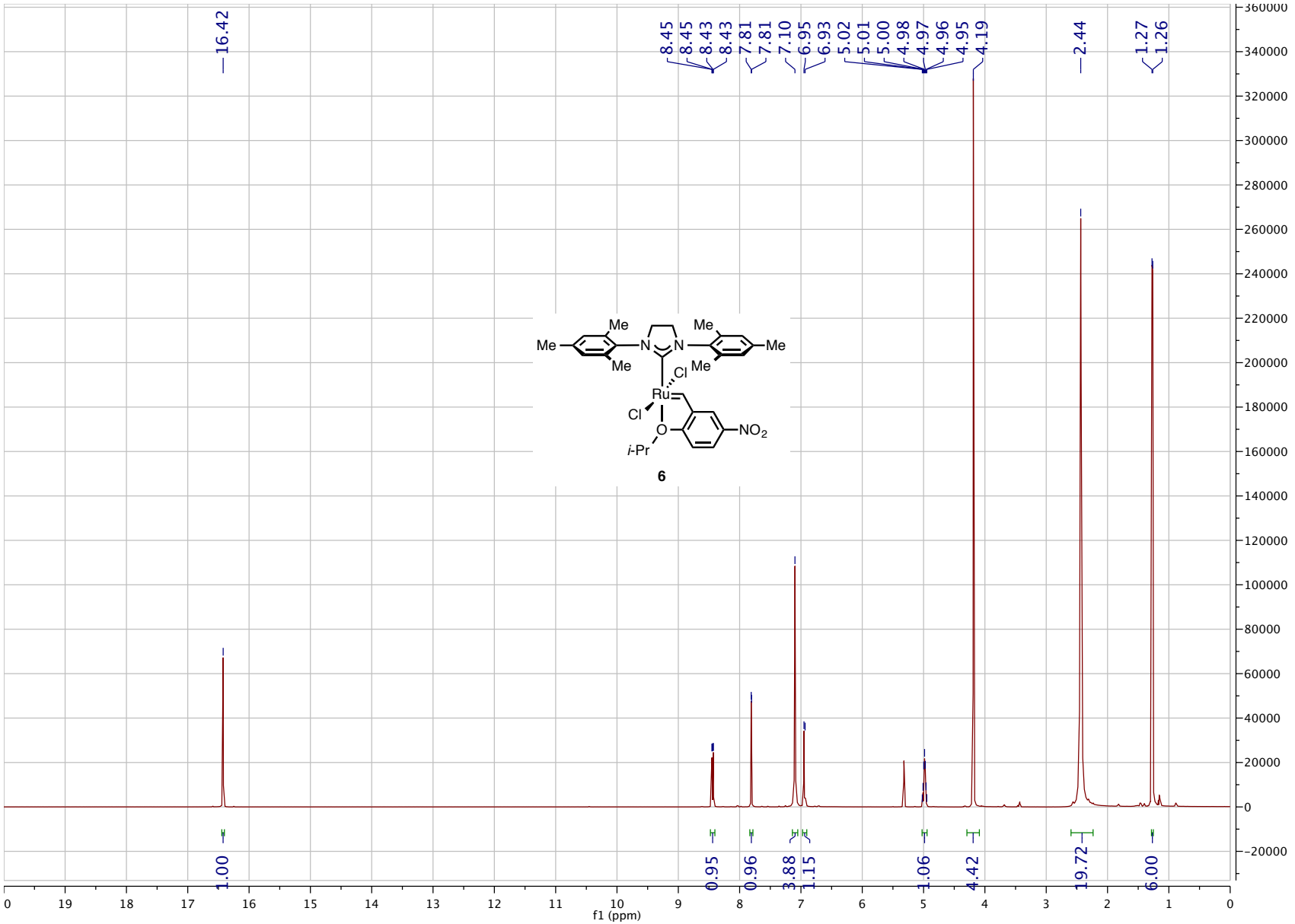
133.64
131.93
129.74
129.46
128.91
128.19
123.96
121.77
77.91
51.94
21.38
20.53
18.65
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
i-Pr
5
f1 (ppm)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7.81
7.10
6.95
6.93
5.02
5.01
5.00
4.98
4.97
4.96
4.95
4.19
2.44
1.27
1.26
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
NO2
i-Pr
6
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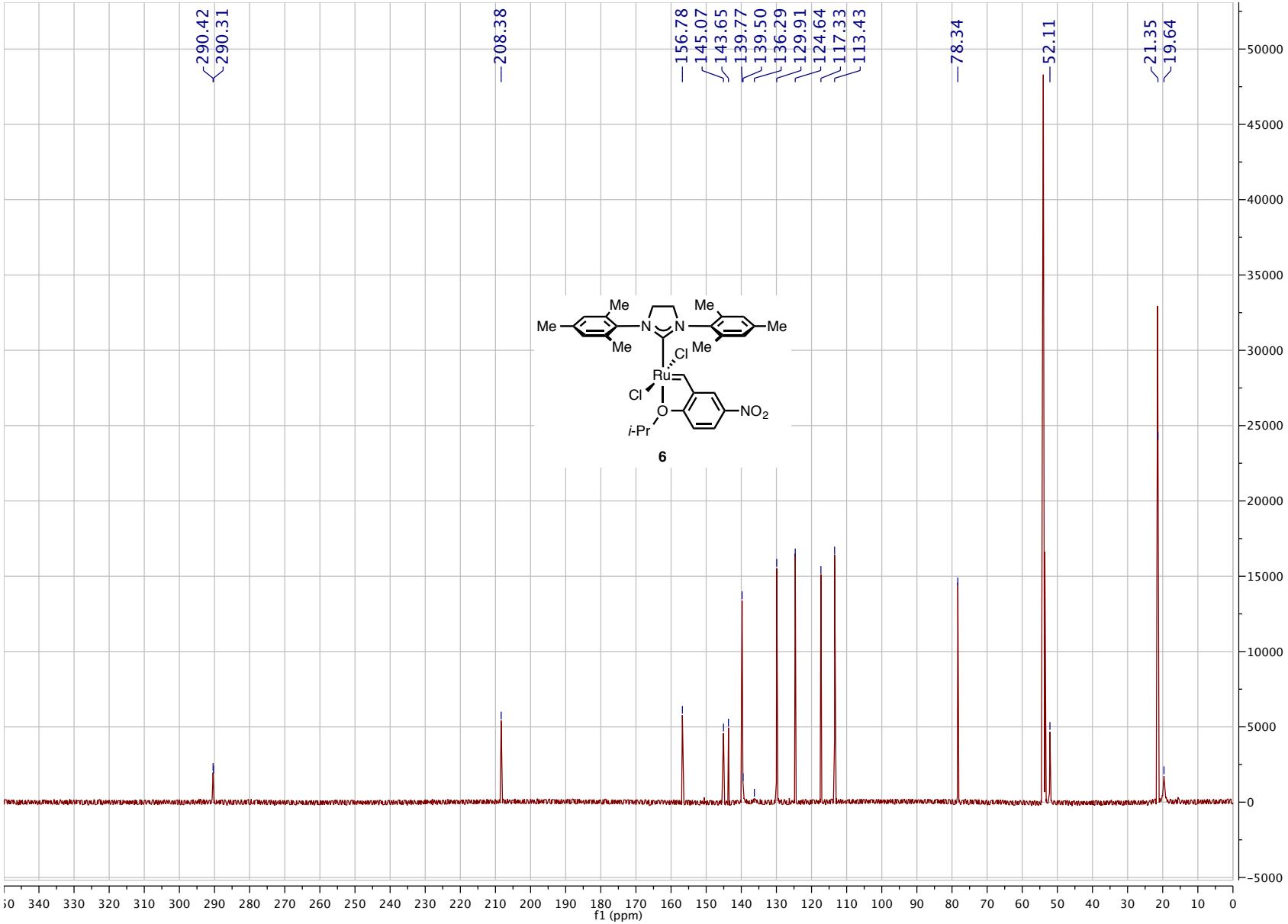
3.88
1.15
1.06
4.42
19.72
6.00
f1 (ppm)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208.38
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143.65
139.77
139.50
136.29
129.91
124.64
117.33
113.43
78.34
52.11
21.35
19.64
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Me
Me
Me
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N
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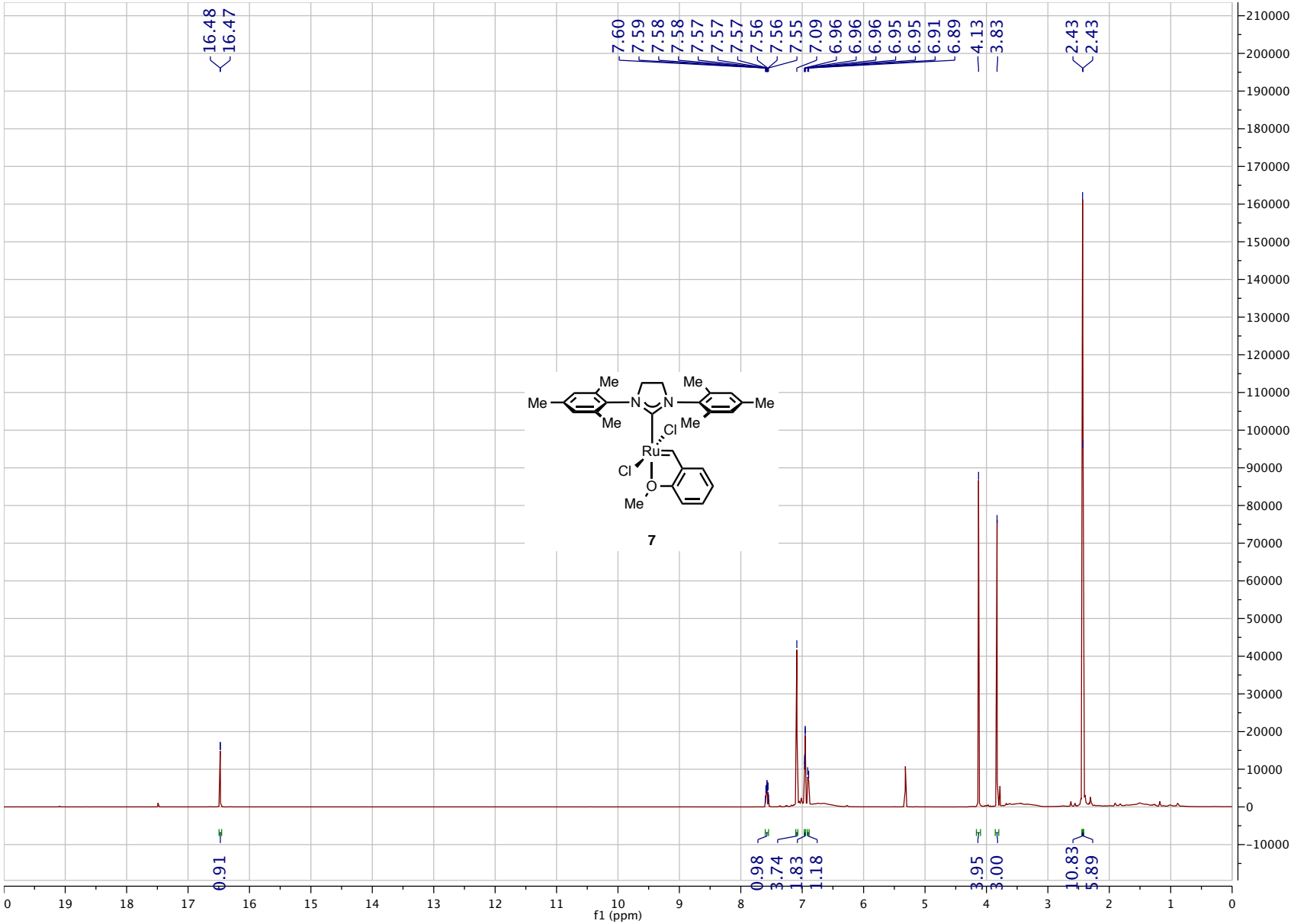
Cl
O
NO2
i-Pr
6
f1 (ppm)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16.47
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7.57
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7.56
7.56
7.55
7.09
6.96
6.96
6.96
6.95
6.95
6.91
6.89
4.13
3.83
2.43
2.43
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
Me
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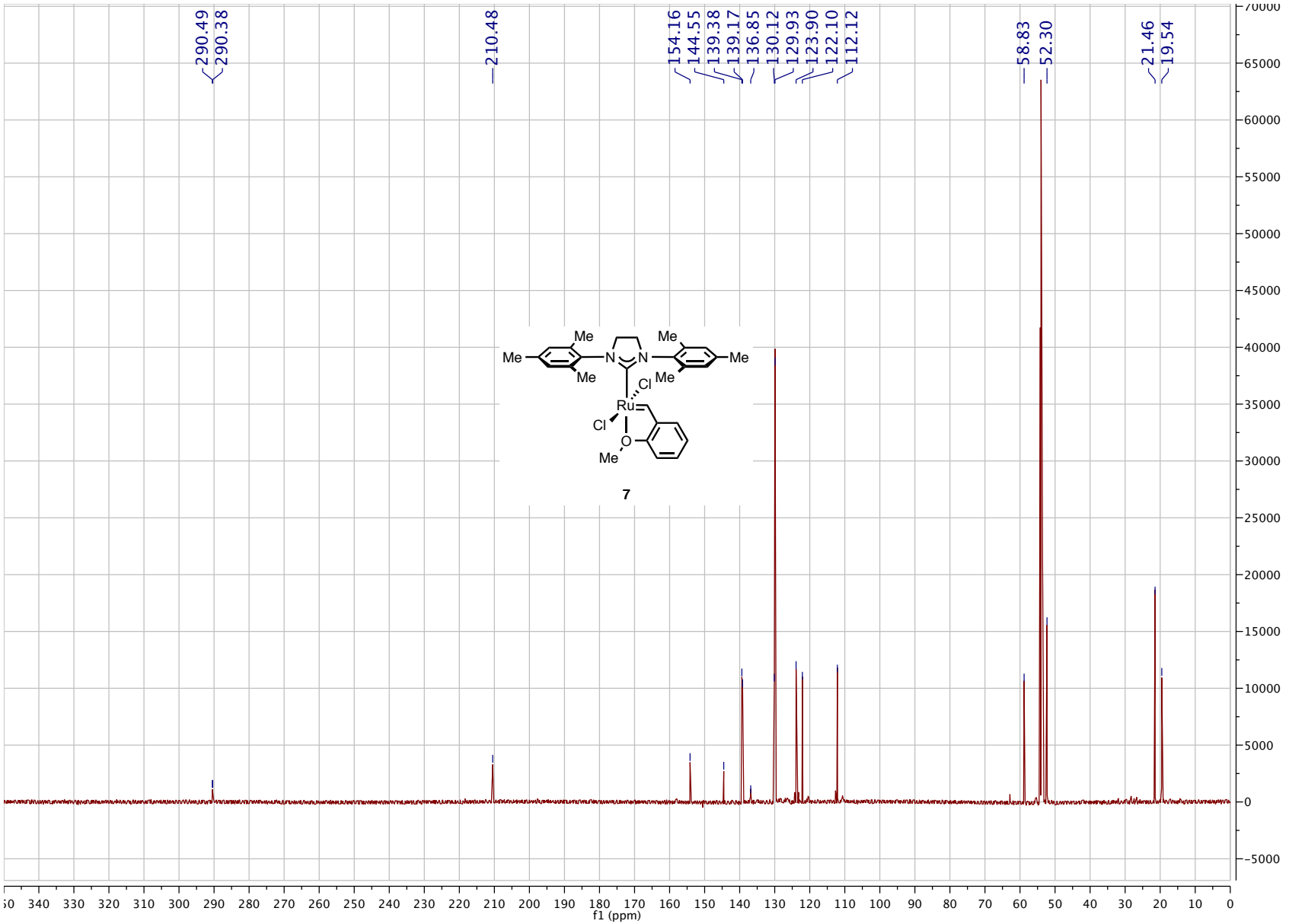
0.98
3.74
1.83
1.18
3.95
3.00
10.83
5.89
f1 (ppm)

7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290.38
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154.16
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139.38
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136.85
130.12
129.93
123.90
122.10
112.12
58.83
52.30
21.46
19.54
Me
Me
Me
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Me
Me
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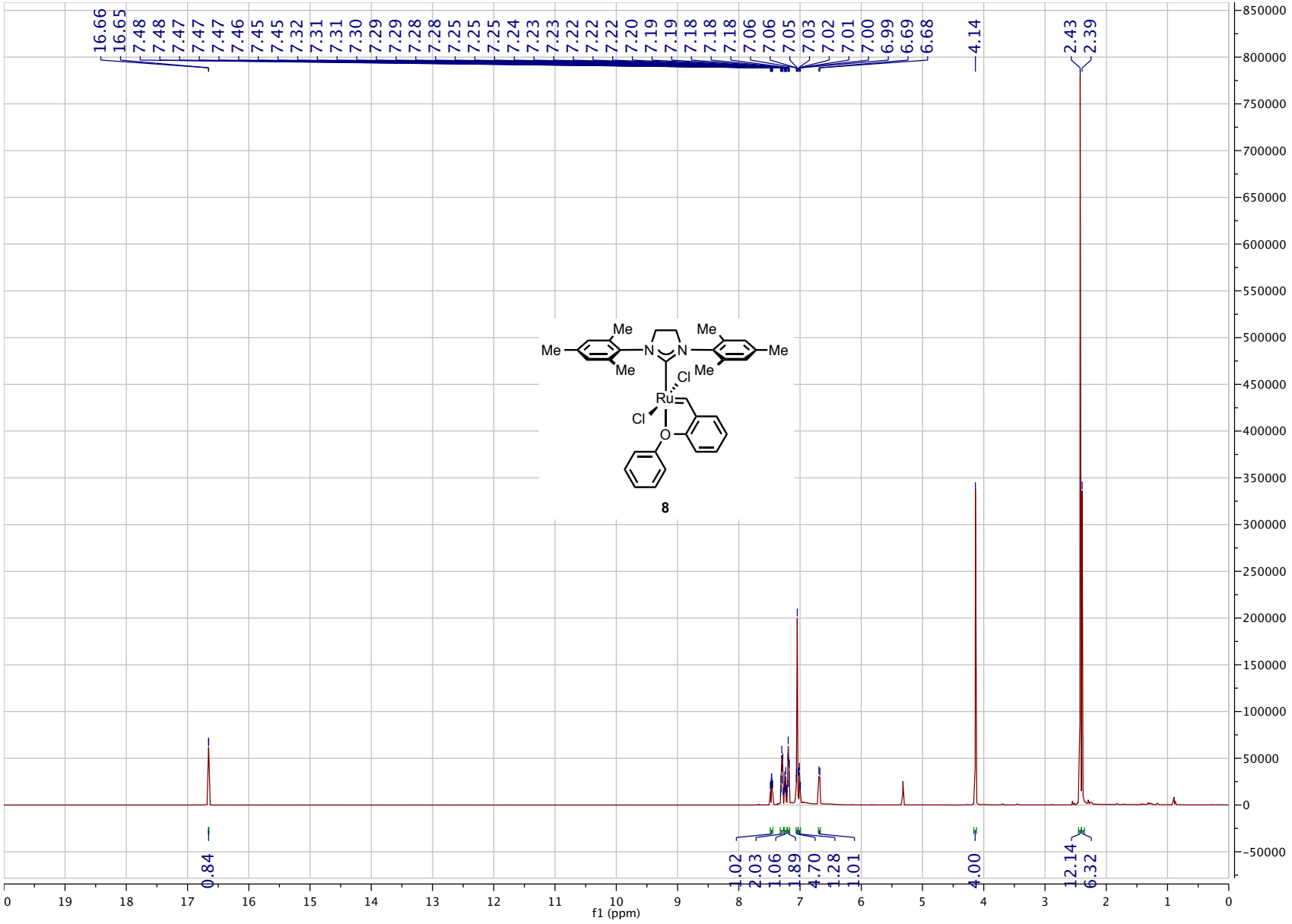
N
Cl
Ru
Cl
O
Me
7
f1 (ppm)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7.47
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7.46
7.45
7.45
7.32
7.31
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7.30
7.29
7.29
7.28
7.28
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.22
7.20
7.19
7.18
7.18
7.18
7.06
7.06
7.05
7.03
7.02
7.01
7.00
6.99
6.69
6.68
4.14
2.43
2.39
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
8
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1.06
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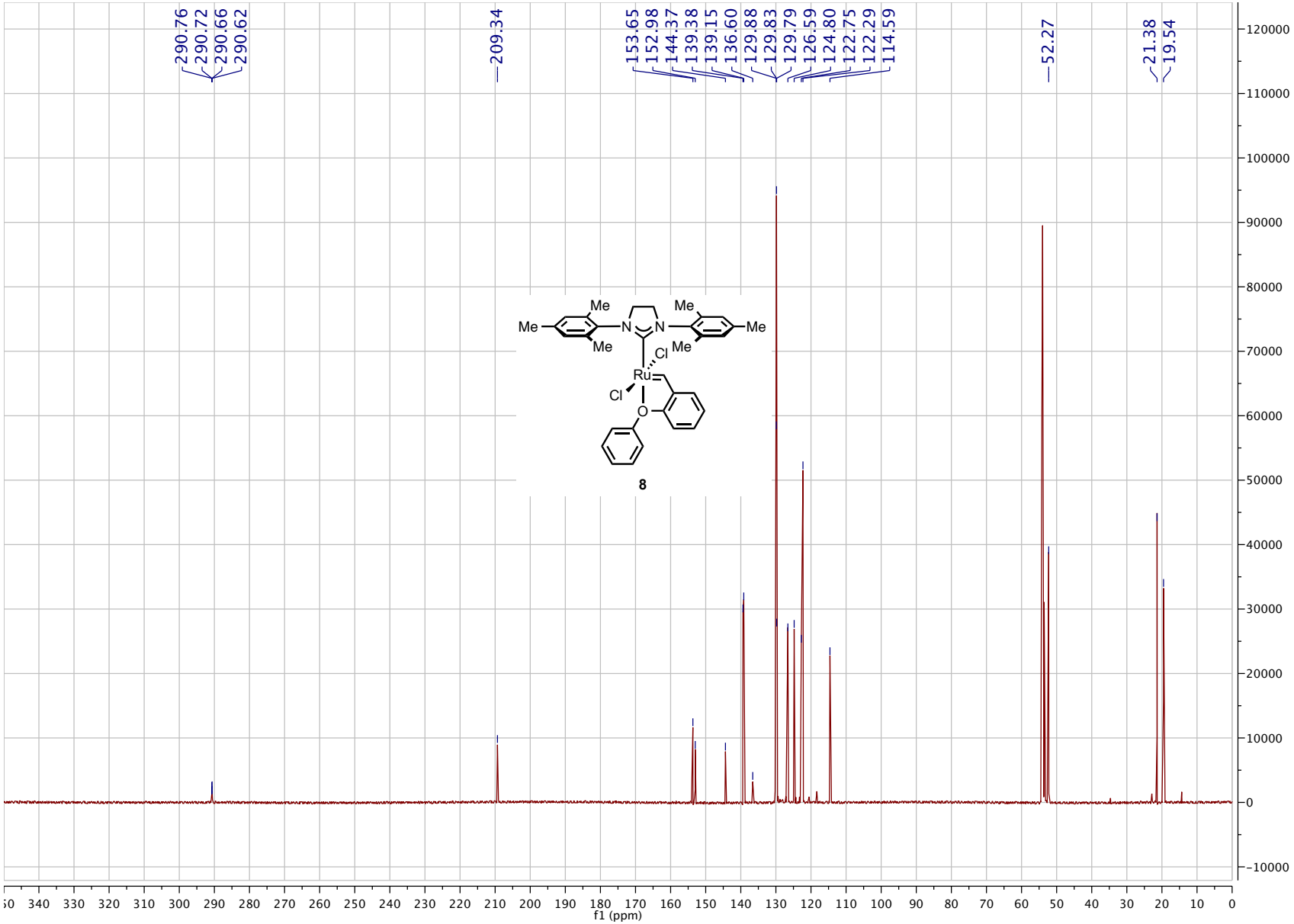
1.28
1.01
4.00
12.14
6.32
f1 (ppm)


290.76
290.72
290.66
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209.34
153.65
152.98
144.37
139.38
139.15
136.60
129.88
129.83
129.79
126.59
124.80
122.75
122.29
114.59
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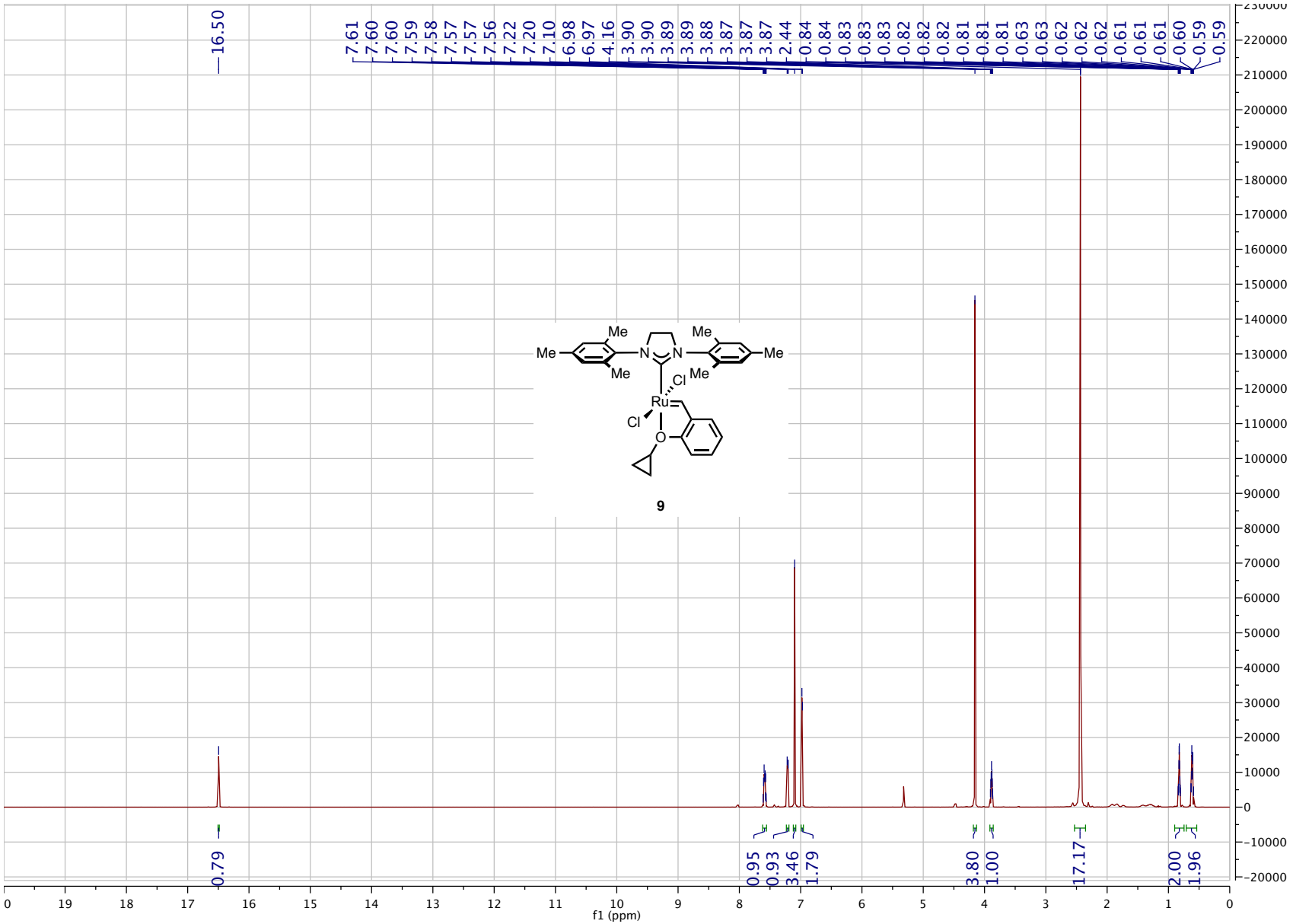
N
Cl
Ru
Cl
O
8
f1 (ppm)


16.50
7.61 7.60 7.60 7.59 7.58 7.57 7.57 7.56 7.22 7.20 7.10 6.98 6.97 4.16 3.90 3.90 3.89 3.89 3.88 3.87 3.87 3.87 2.44 0.84 0.84 0.83 0.83 0.82 0.82 0.82 0.81 0.81 0.81 0.63 0.63 0.62 0.62 0.62 0.61 0.61 0.61 0.60 0.59 0.59
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
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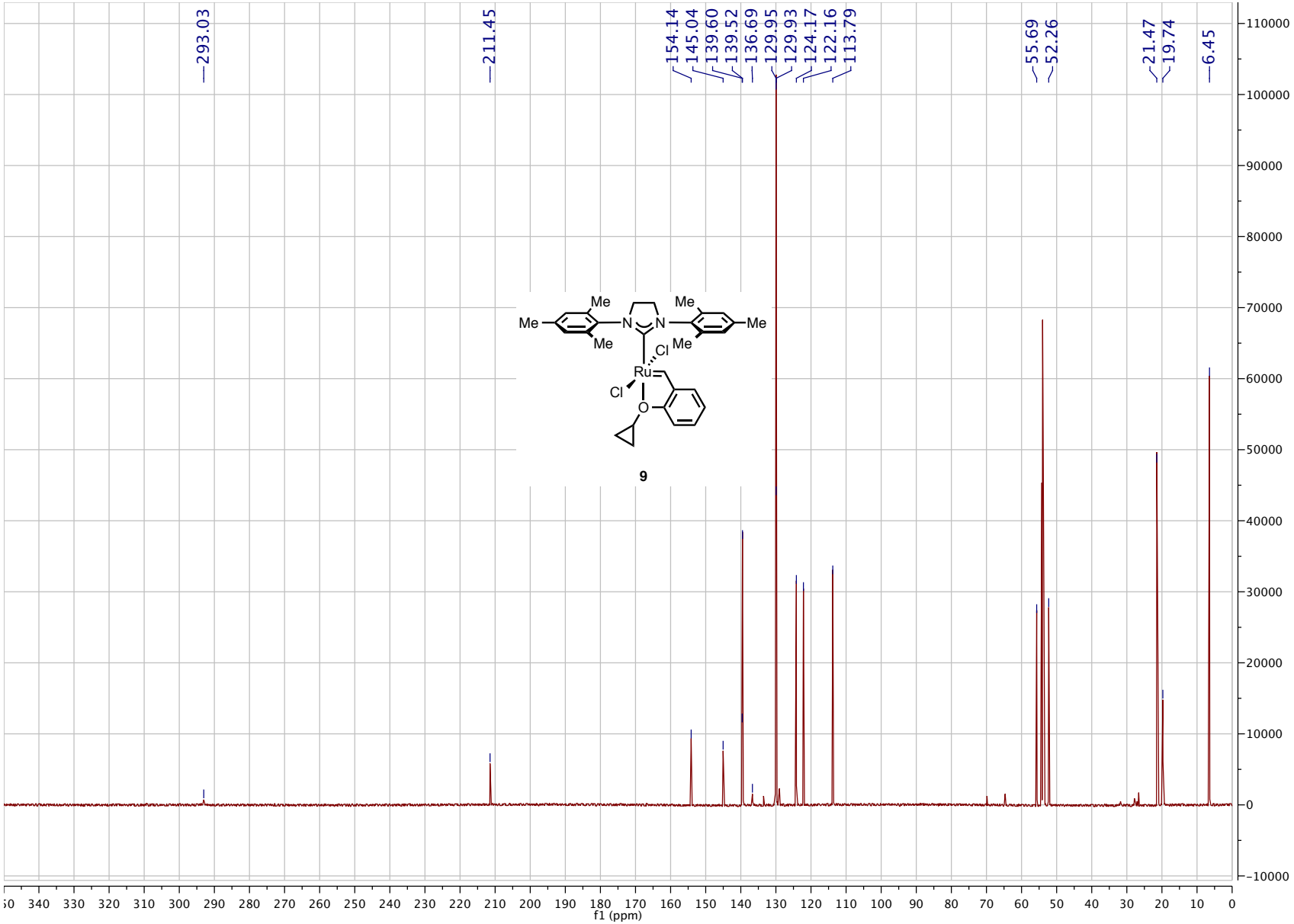
0.95
0.93
3.46
1.79
3.80
1.00
17.17
2.00
1.96
f1 (ppm)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211.45
154.14
145.04
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139.52
136.69
129.95
129.93
124.17
122.16
113.79
55.69
52.26
21.47
19.74
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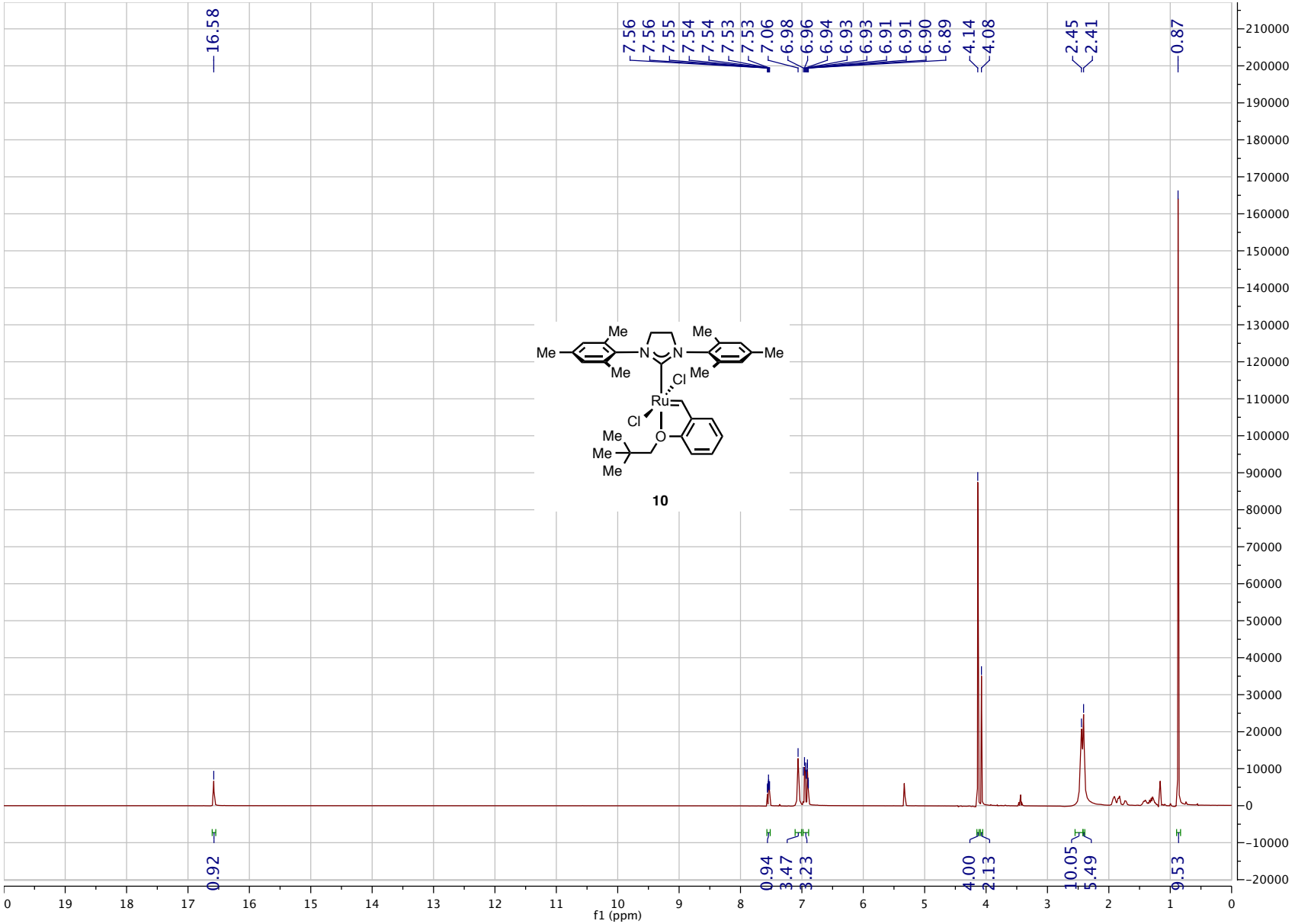
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
9
f1 (ppm)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7.54
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7.53
7.06
6.98
6.96
6.94
6.93
6.93
6.91
6.91
6.90
6.89
4.14
4.08
2.45
2.41
0.87
Me
Me
Me
N
N
Me
Me
Me
Cl
Ru
Cl
O
Me
Me
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10
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0.94
3.47
3.23
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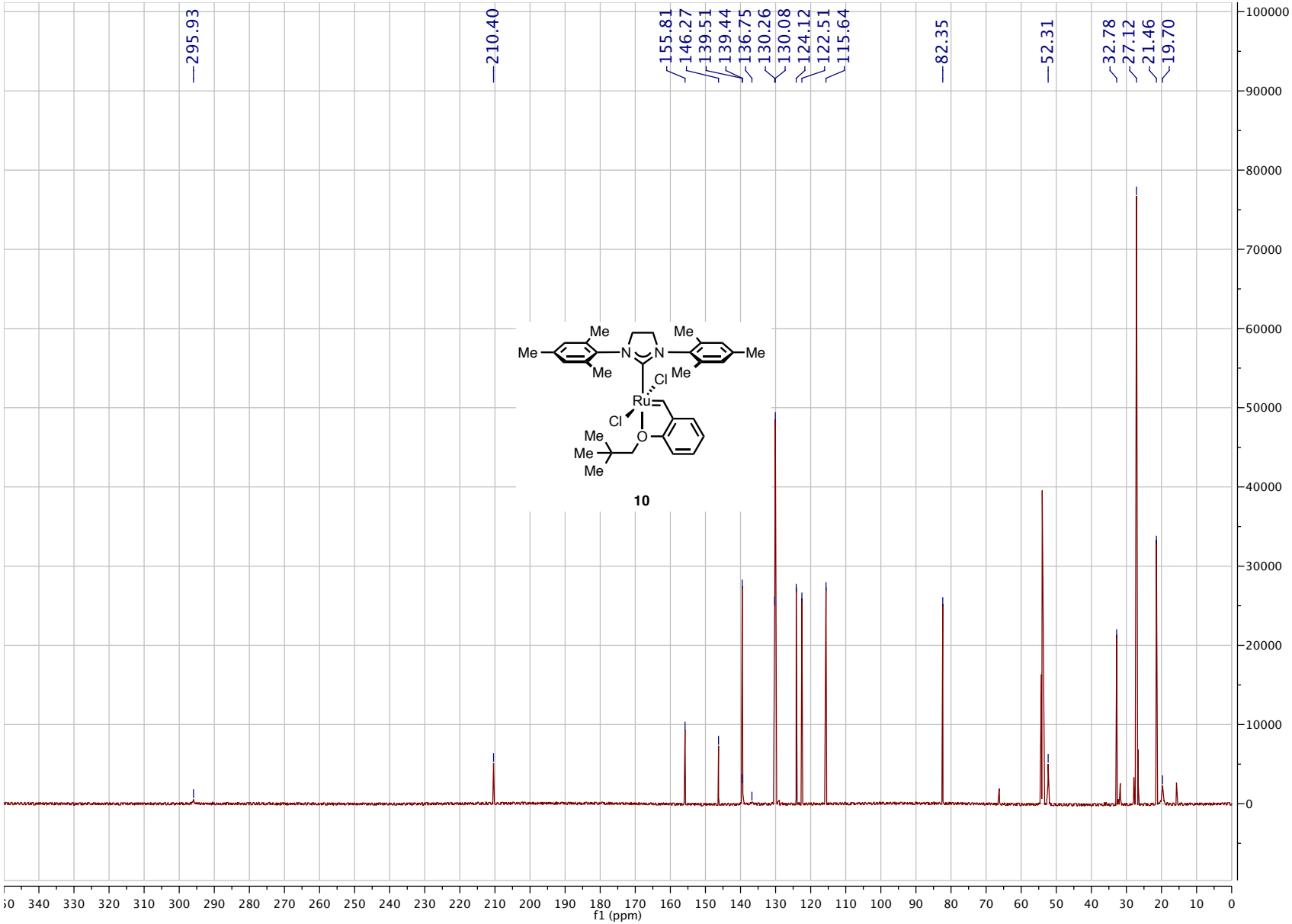
10.05
5.49
9.53
f1 (ppm)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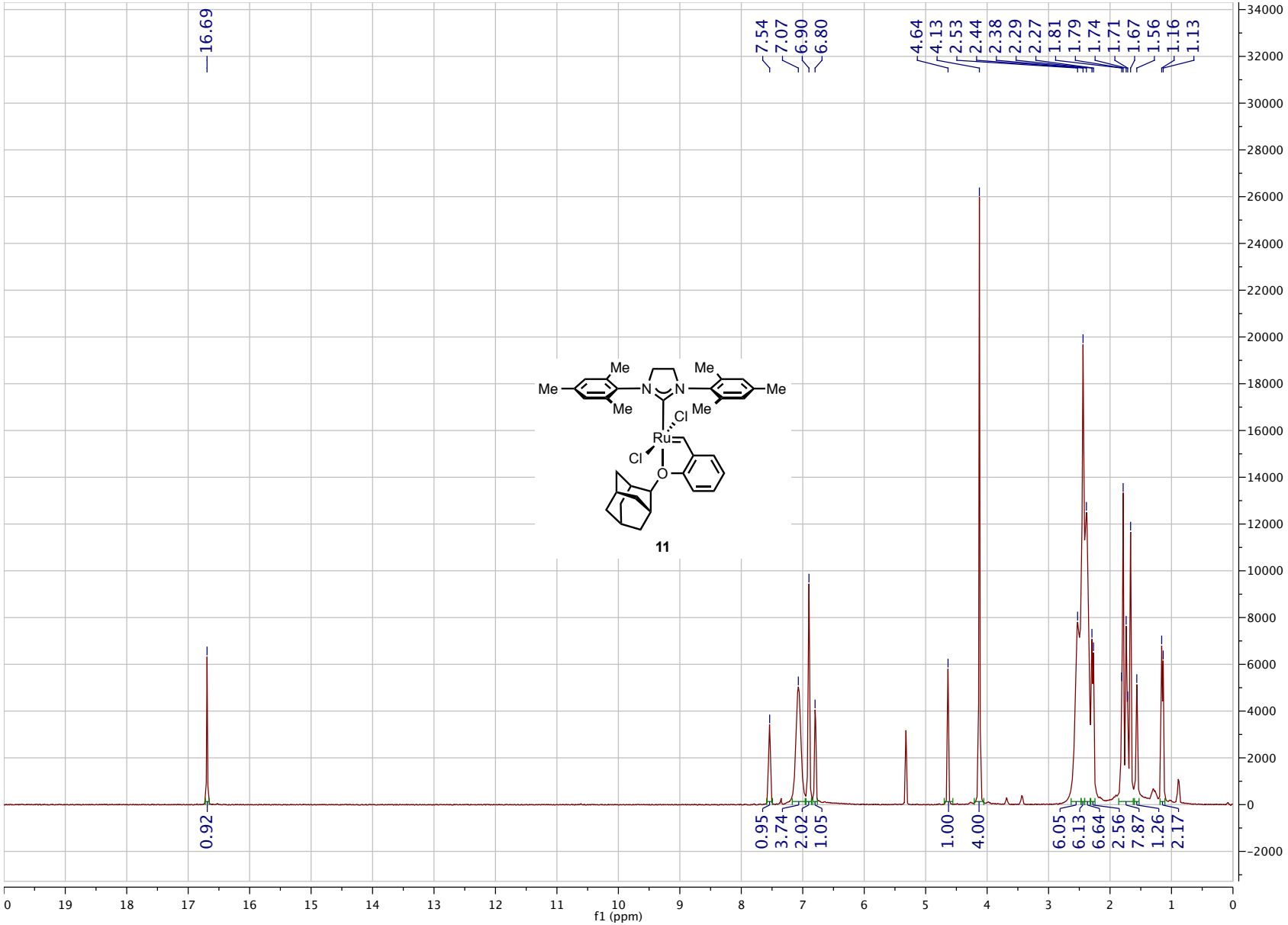
155.81
146.27
139.51
139.44
136.75
130.26
130.08
124.12
122.51
115.64
82.35
52.31
32.78
27.12
21.46
19.70
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
Me
Me
Me
10
f1 (ppm)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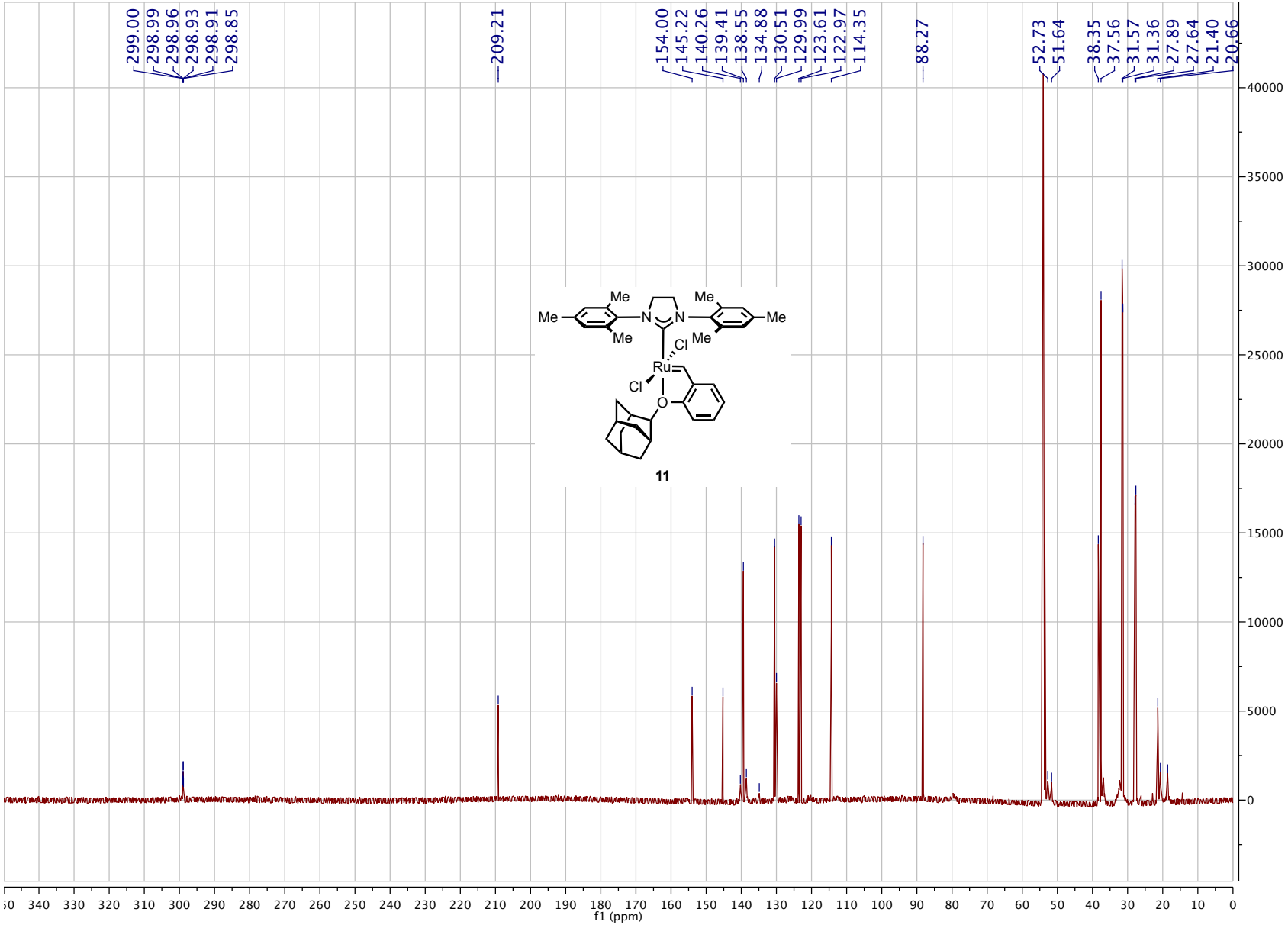
4.64
4.13
2.53
2.44
2.38
2.29
2.27
1.81
1.79
1.74
1.71
1.67
1.56
1.16
1.13
0.92
0.95
3.74
2.02
1.05
1.00
4.00
6.05
6.13
6.64
2.56
7.87
1.26
2.17
f1 (ppm)
Me
N
Ru
Cl
O
11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140.26
139.41
138.55
134.88
130.51
129.99
123.61
122.97
114.35
88.27
52.73
51.64
38.35
37.56
31.57
31.36
27.89
27.64
21.40
20.66
Me
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Me
Me
Me
Me
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Ru
Cl
O
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35000
30000
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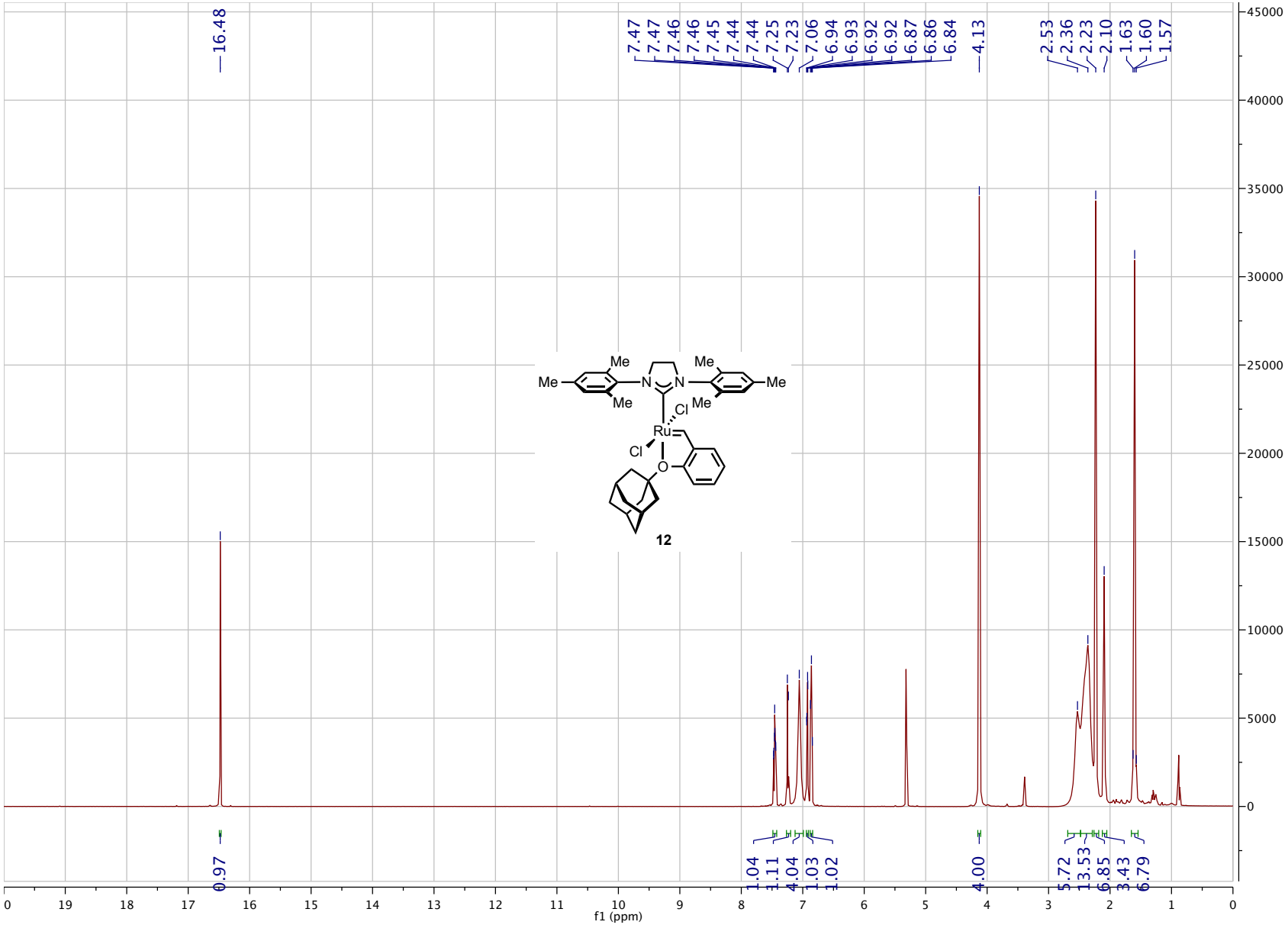
20000
15000
10000
5000
0
f1 (ppm)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7.47
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7.44
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7.06
6.94
6.93
6.92
6.92
6.87
6.86
6.84
4.13
2.53
2.36
2.23
2.10
1.63
1.60
1.57
Me
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
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1.11
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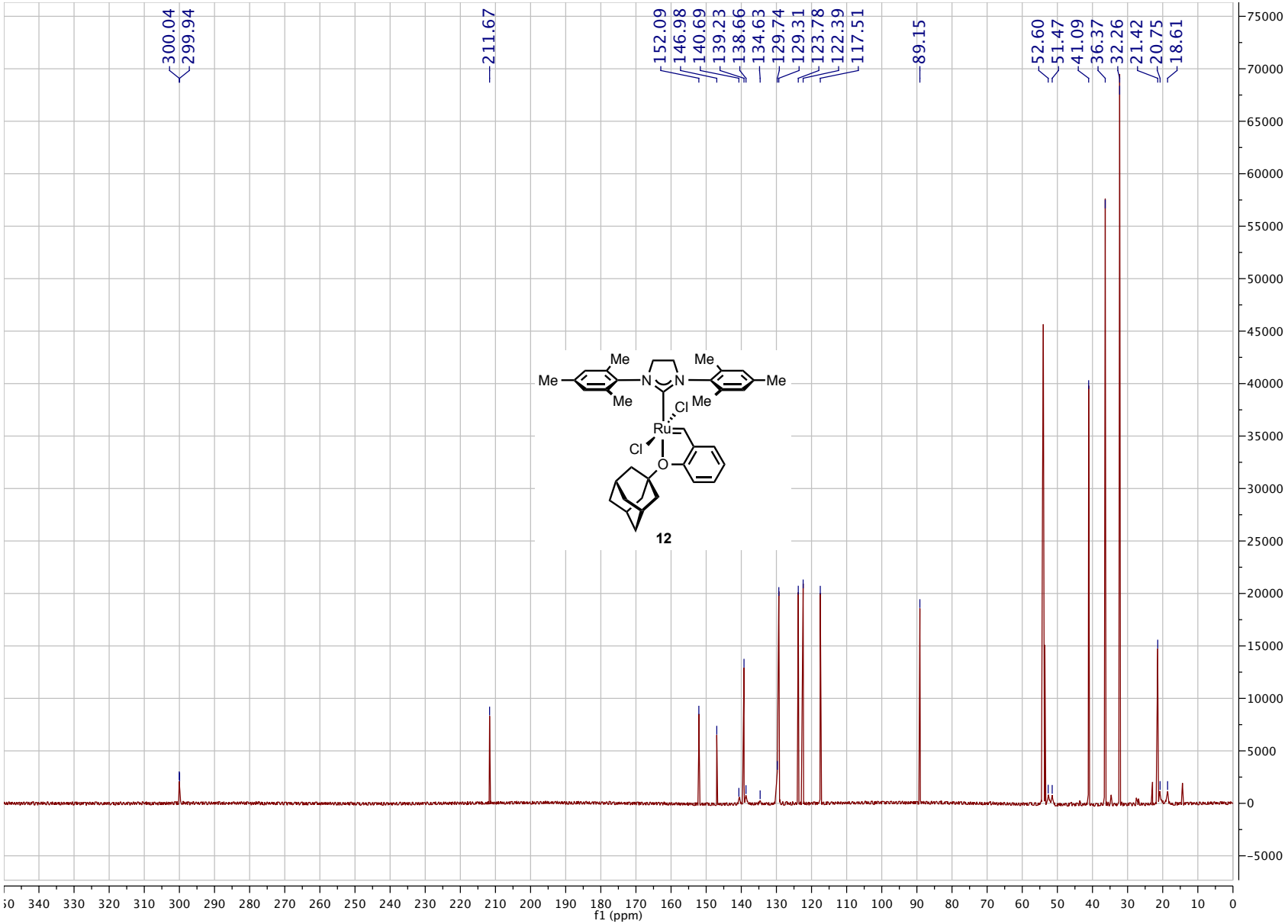
1.03
1.02
4.00
5.72
13.53
6.85
3.43
6.79
f1 (ppm)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138.66
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129.74
129.31
123.78
122.39
117.51
89.15
52.60
51.47
41.09
36.37
32.26
21.42
20.75
18.61
Me
Me
Me
Me
Me
N
N
Cl
Ru
Cl
O
12
f1 (ppm)